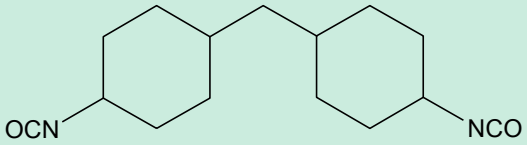
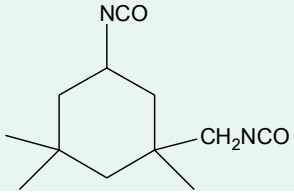
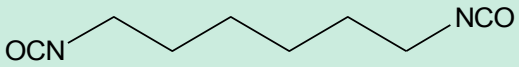
Wannate HMDI

Building Block for High Performance Polyurethanes

Yantai Wanhua Polyurethanes Co., Ltd

Contents

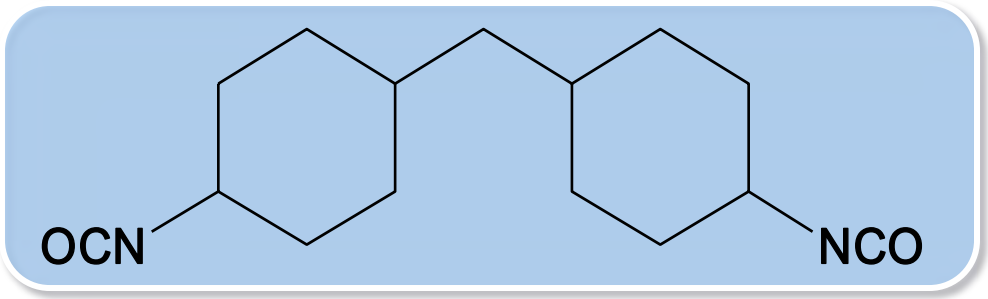
Aliphatic Diisocyanate

	Structure Formula	M_w	NCO%	Bp/℃	Reactivity	Isomer Type
HMDI		262	32.1	180	Low	3
IPDI		222	37.8	117	Medium	2
HDI		168	50	82	Relatively High	1

- High mechanical performance
- Outstanding chemical stability
- Excellent yellowing resistance

Contents

Wannate HMDI

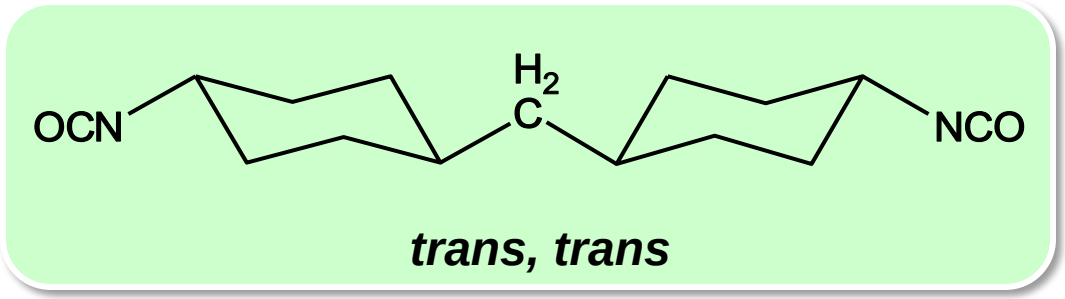


Bis(4-isocyanato cyclohexyl) methane

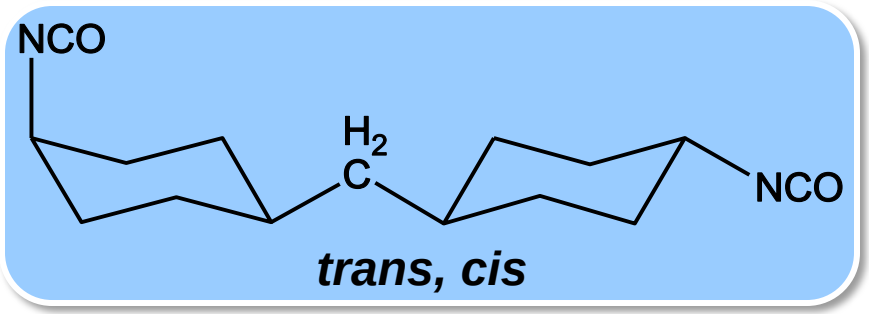
Abbr.: HMDI H_{12}MDI RMDI PICM

Molecular Formula: $C_{15}H_{22}N_2O_2$

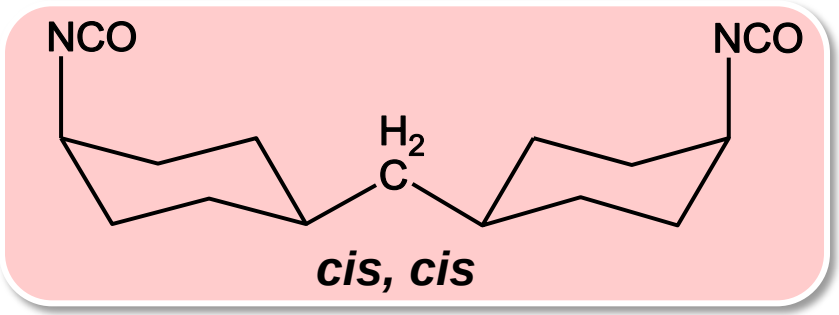
Stereoisomers of HMDI



trans, trans



trans, cis



cis, cis

- ***Trans, trans*** **isomer has strong influence on the properties**
- ***Trans, trans*** **isomers offer ordered structure and improved properties**
- **Above 24%, *trans, trans* isomers tend to crystallize out of solution under low temperature**

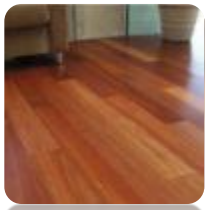
Wannate HMDI VS. Competitors

Spec.	Wannate HMDI	Comp. A	Comp. B
Trans, trans/%	< 24 (16 ~ 22)	< 24 (16 ~ 24)	< 24 (15 ~ 24)
2,4-isomer/%	< 0.3	> 8	> 12
NCO%	32.05	32.02	31.95

Wannate HMDI: Same processability; potential unique properties

Application of Wannate HMDI

- Elastomer
- Waterborne Dispersion
- Coating
- Adhesive
- Sealant




Contents

Production Status for Wannate HMDI

Technology

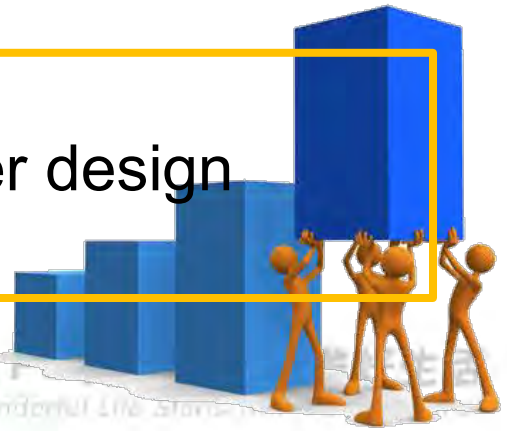
- Independently developed MDA hydrogenation technology
- No. 1 MDA manufacturer in A/P region

Current Production

- HMDA capacity in Yantai is 4000 t/year
- HMDI capacity in Ningbo is 4000 t/year

Future Plan

- 15000 t/year HMDI facility in Yantai is under design
- Plan to start-up in 2014

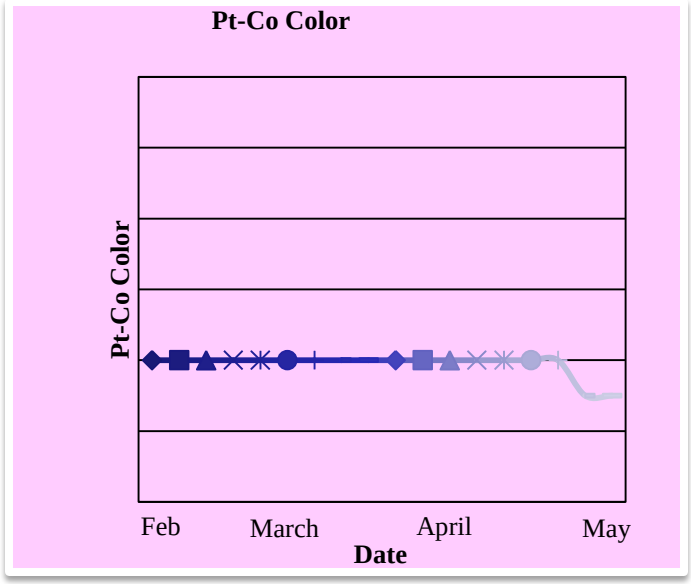


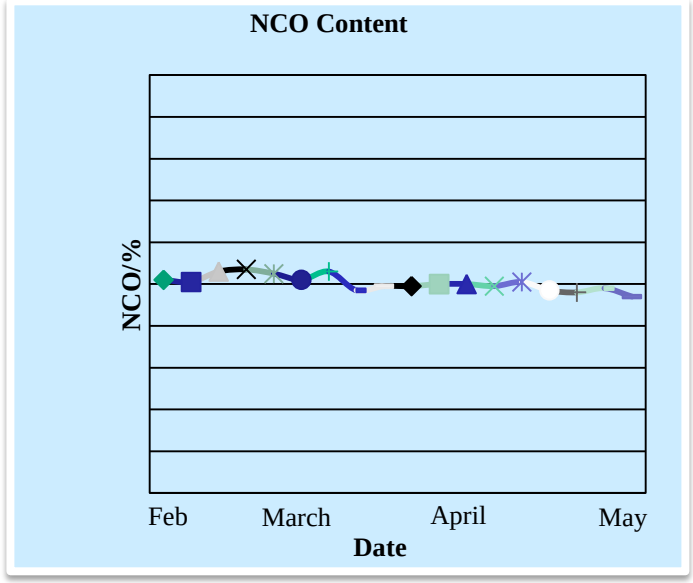
Specifications for Wannate HMDI

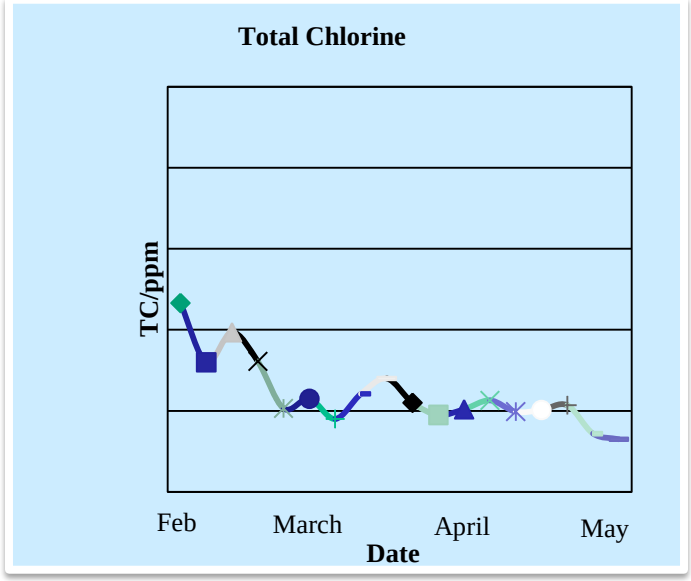
	specification	Method
Purity/%	≥ 99.5	GC
NCO/%	≥ 31.8	GB 12009.4
Color (Pt-Co)	≤ 30	GB 3143
Solidifying point/℃	≤ 20	GB 7533
Density (20℃) / (g/cm^3)	≈ 1.07	GB 4472
Trans, trans ratio/%	≤ 24%	GB/T 261
Viscosity (25℃) / (mPa.s)	≈ 30	GB 12009.3
Hydrolyzable chlorides/ppm	≤ 10	GB 12009.2
Total chlorides/ppm	≤ 1000	Internal method

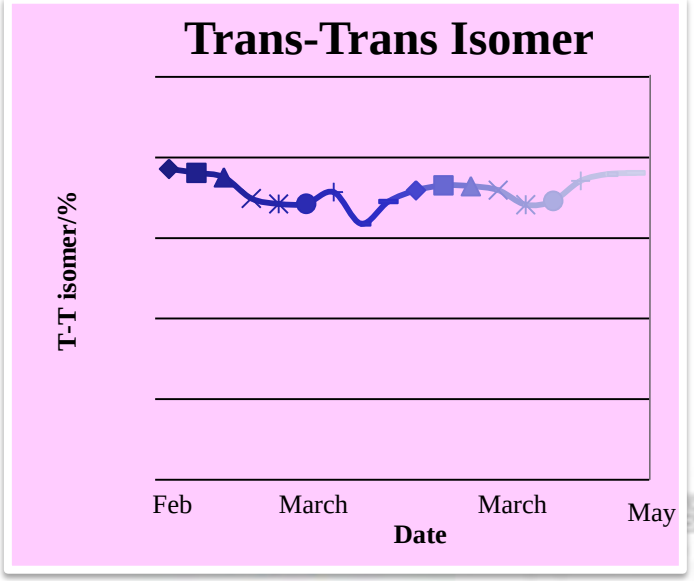
Ready as a drop-in replacement

Wannate HMDI Quality Control



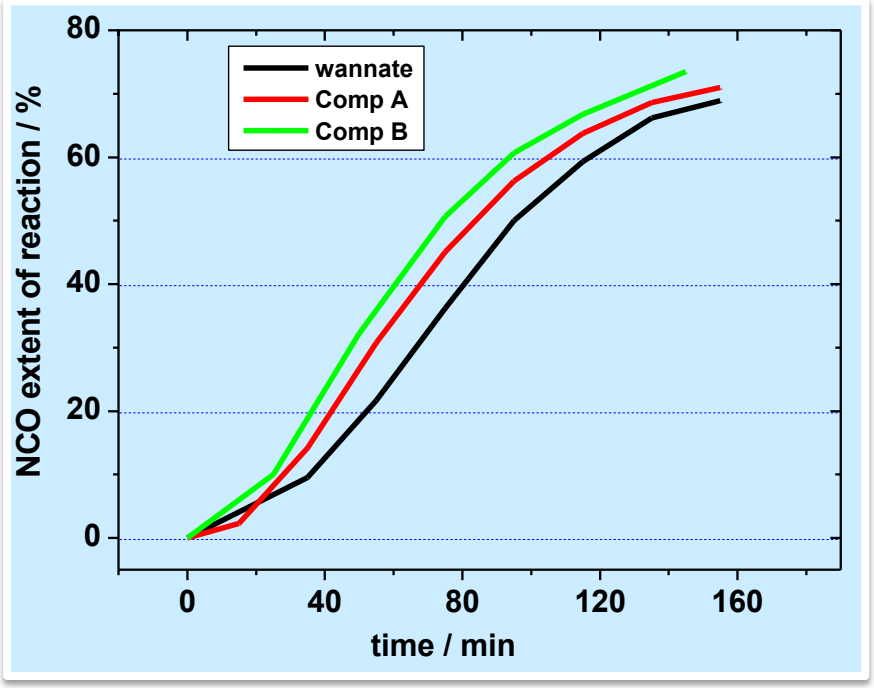






Contents

Wannate HMDI---Reactivity



Iso-Polyol prepolymer

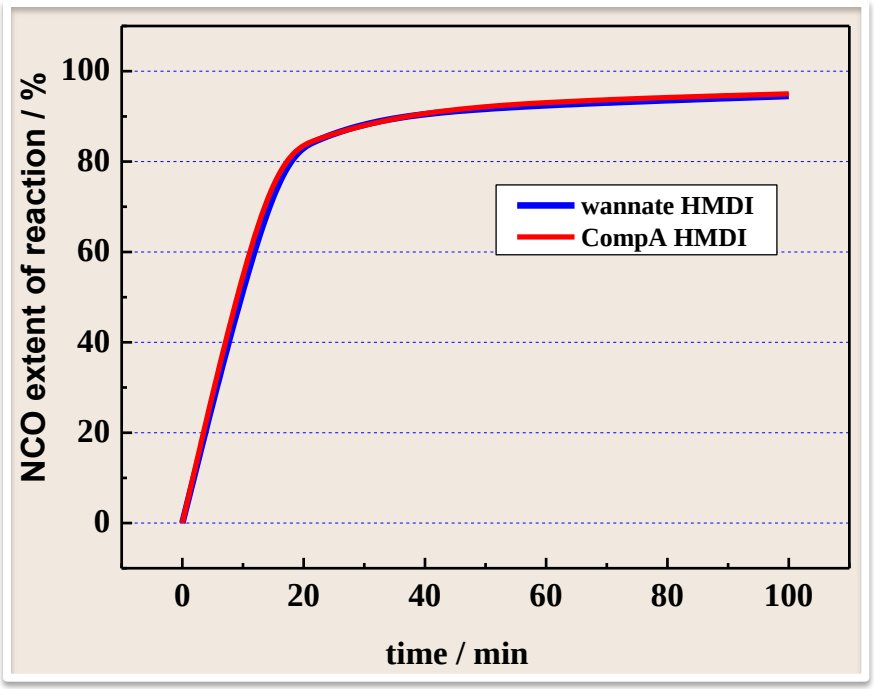
-NCO/-OH = 2

Temperature: 90 ℃

No catalyst

- **Reactivity similar to competitors'**
- **Gentle and controllable reaction process**
- **Possibility of polymer structure design**

Wannate HMDI---Reactivity



Iso-Polyol prepolymer

-NCO/-OH = 2

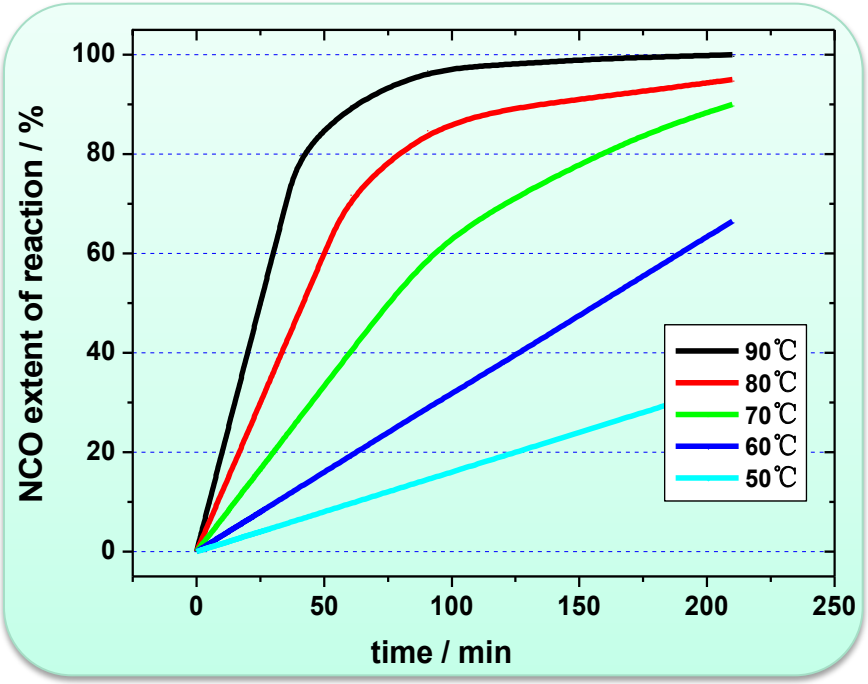
Temperature: 70 ℃

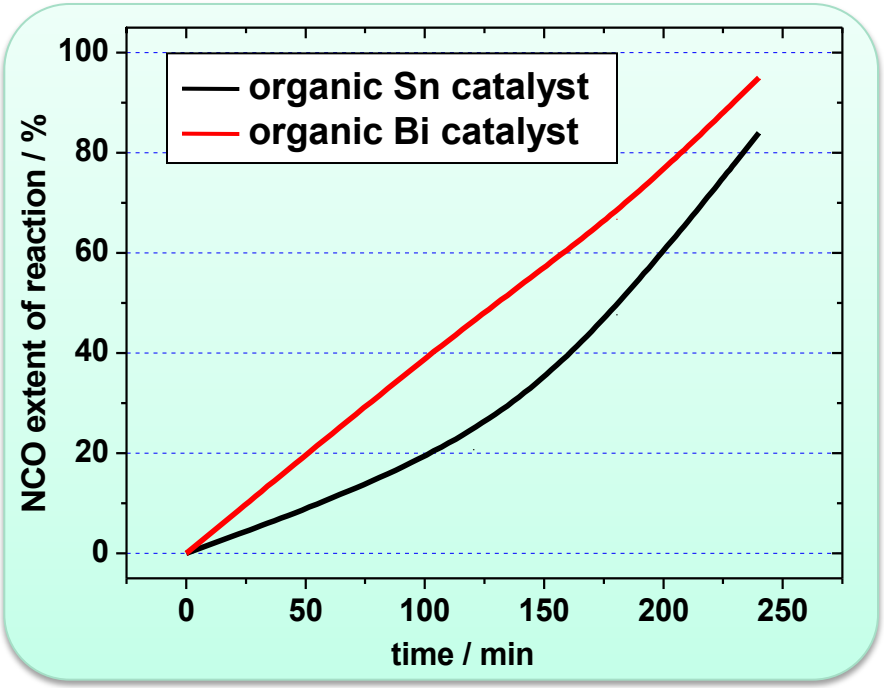
Sn Catalyst: 400 ppm

- **Reactivity can be adjusted through addition of proper catalyst system**

Wannate HMDI---Reactivity

HMDI + PPG-1000 prepolymer





Sn catalyst: 500 ppm

Temperature: 80 ℃

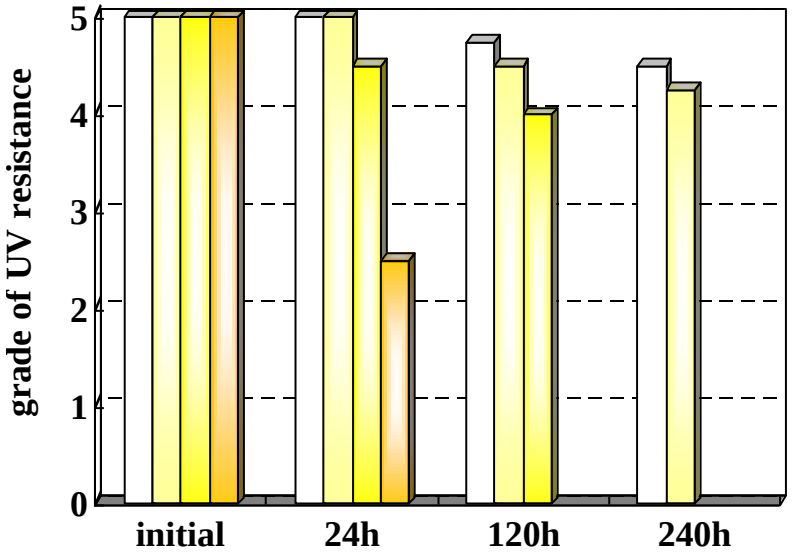
Recommended temperature:

70 ~ 90 ℃

Reactivity:

Bi catalyst＞ Sn catalyst

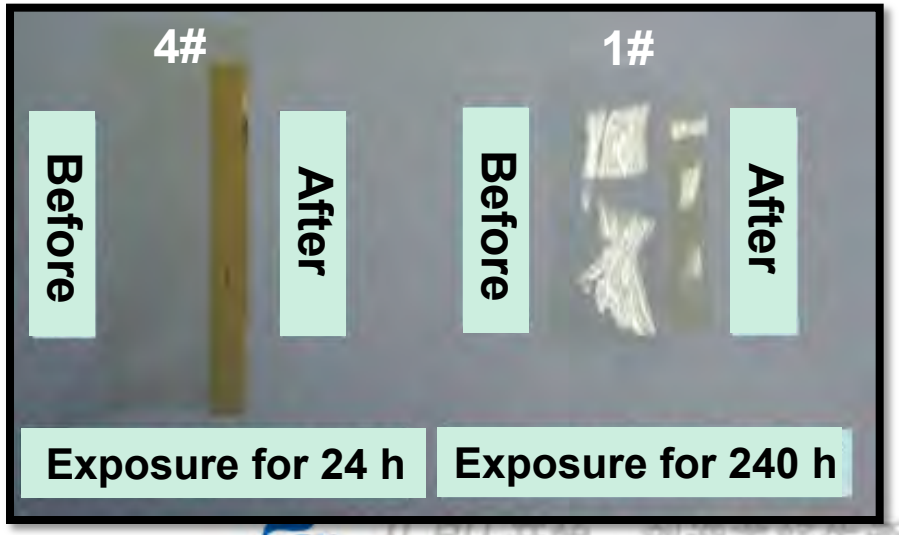
Wannate HMDI---Yellowing Resistance



- Wannate HMDI + PTMEG1000
- Comp. A HMDI + PTMEG1000
- IPDI + PTMEG1000
- WH-MDI50 + PTMEG1000

Testing condition:
300 W xenon lamp; 50 ℃

- **Without aromatic group**
- **Excellent anti-yellowing property**



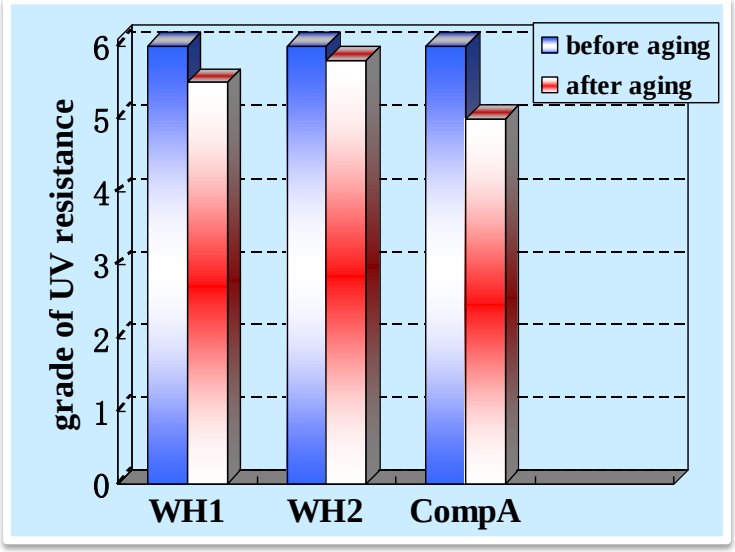
Wannate HMDI---Aging Resistance

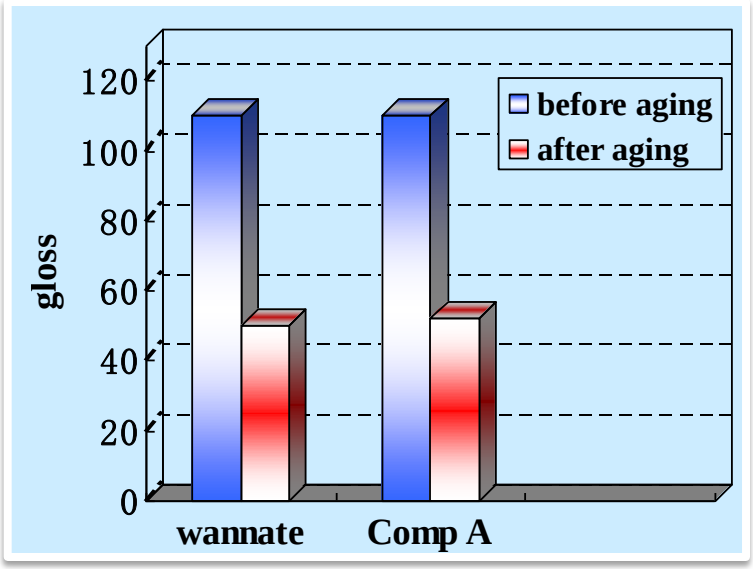
WH1 (Wannate HMDI + PCDL1000)

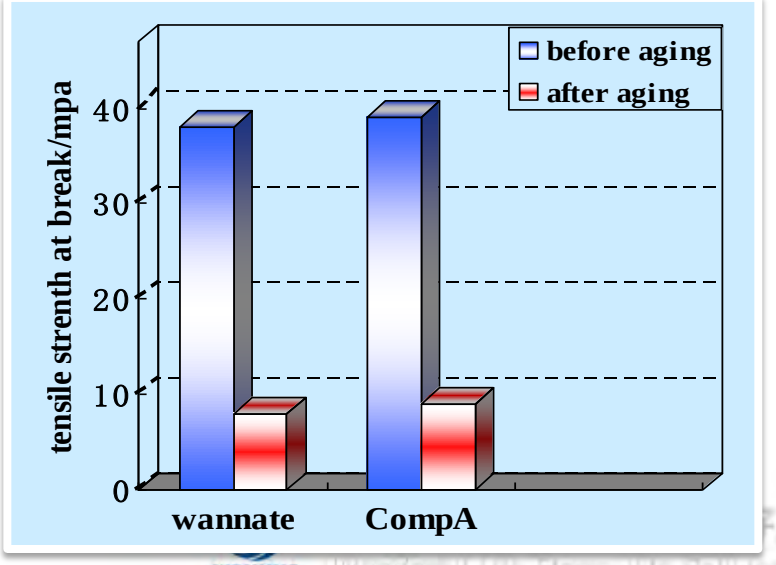
WH2 (Wannate HMDI + PTMEG1000)

Comp. A (Comp. A + PTMEG1000)

Testing condition:
300 W xenon lamp; 50 ℃;
saturated water vapor pressure

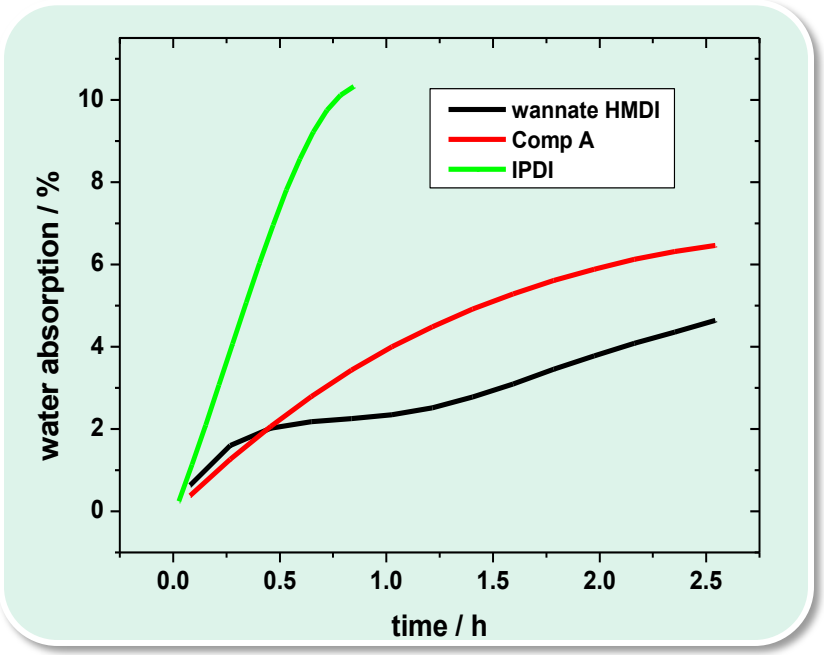


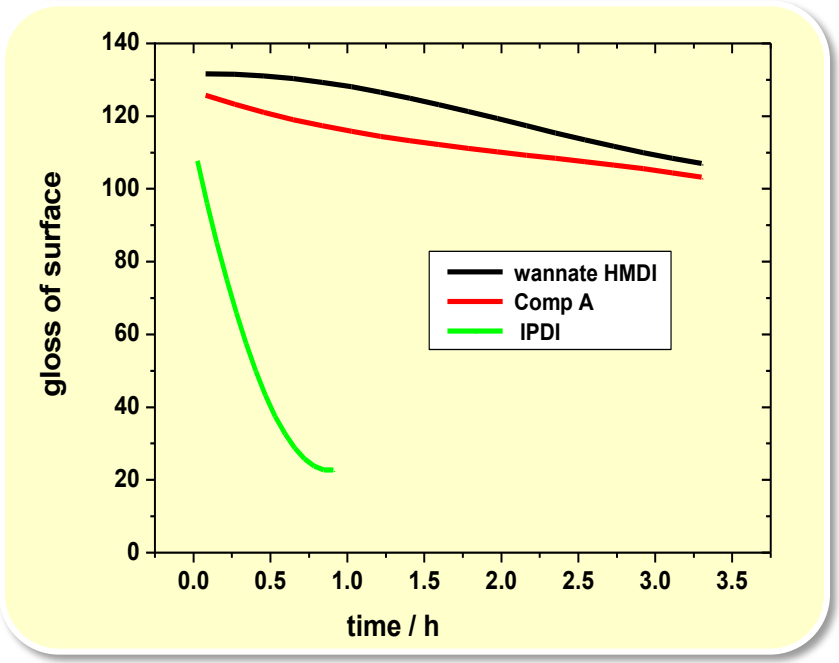




Wannate HMDI---Hydrolysis Resistance

Advantage of HMDI over IPDI



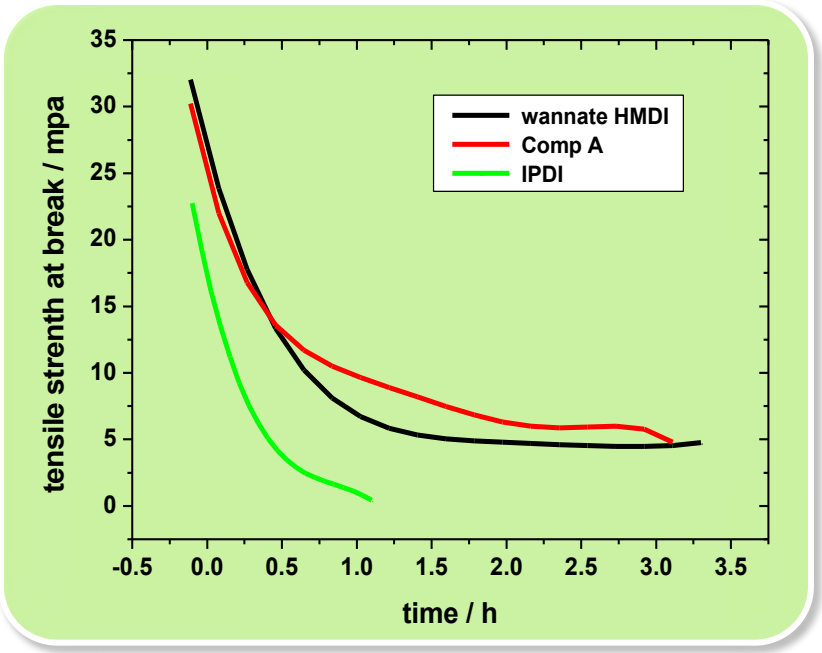


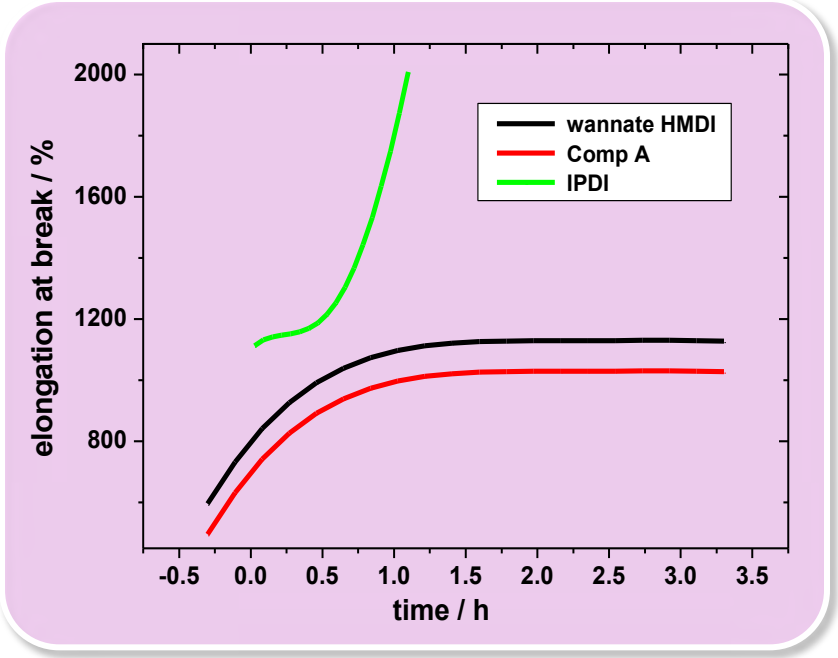
Water absorption

Surface gloss

Waterborne PU film immersed into water (25 ℃)

Wannate HMDI---Hydrolysis Resistance





Tensile strength at break

Elongation at break

Wannate HMDI offers better gloss preservation and hydrolysis resistance than IPDI.

Wannate HMDI---Application Performance

▶▶ Waterborne PU system

Comparison of Mechanical Properties

	Wannate HMDI	Comp. 1
Tensile strength at break/Mpa	26.8	24.3
Elongation at break/%	820	710
100% tensile strength/Mpa	9	8
200%tensile strength/MPa	12	9.5

Wannate HMDI---Application Performance

▶ Solvent-based PU system

Comparison of Mechanical Properties

	Wannate HMDI	Comp. 1	Comp. 2
Tensile strength at break/Mpa	39.97	41.5	40.3
Elongation at break/%	820	770	840
100% tensile strength/MPa	6	6	6
300% tensile strength/Mpa	12	12	12

HMDI + PTMG1000 + BDO

Wannate HMDI---Application Performance

➤ Elastomer

Comparison of Mechanical Properties

	Wannate HMDI	HMDI (includ. 10%2,4-isomer)	Comp. 2
Hardness/A	86	83	78
Tensile strength at break/Mpa	50	51	36
Elongation at break/%	870	850	890
100% tensile strength/MPa	6	3.7	2.5
300%tensile strength/Mpa	9.5	6.7	5.8

Outstanding Quality of Wannate HMDI

Appropriate reaction activity

- Possibility of reaction control and structure design

Outstanding yellowing resistance

- Free of phenyl group enhances anti-yellowing property

Excellent stability and durability

- Stable hexyl group improves chemical durability and weather resistance

High mechanical performance

- Regular structure increases the rigidity of polymer chain

Contents

Customer Feedbacks

▶ Customer 1： Solvent-based PU resin

	Wannate HMDI	Comp. HMDI
Starting sticky time/min	15	10
NCO% (1.5 h)	3.27	3.35
NCO% (2 h)	2.7	2.2
Reaction completed time/h	5	5.25

Conclusion:

Competitor HMDI reacted slightly faster initially; average reaction rates are comparable.

Customer 1: Product performance

	Wannate HMDI	Comp. HMDI
Table abrasion resistance	No obvious abrasion	Obvious abrasion
Tensile strength at break/Mpa	53.16	49.77
Elongation at break/%	932.1	931.8
100% tensile strength/MPa	4.4	4.07
Yellowing resistance index (15 w×2 lamps×4 h)	4.5	4.5
Cold and folding resistance (-20 ℃×80,000 times)	OK	OK
Softening point/℃	183	182
Touch feeling of surface	Slightly wet for competitor HMDI based PU, slightly slippery for Wannate HMDI based PU, smooth, permeability and other properties are comparable	

Customer Feedbacks

▶ Customer 2: Elastomer

	Wannate HMDI	Comp. HMDI
Hardness (LX-A)	87	87
Tear strength/MPa	19	18
Tensile strength at break/MPa	60	53
Elongation at break/%	90	88
Ease of use	OK	OK

Conclusion: Wannate HMDI product can meet the customer's performance requirements.

Summary for Wannate HMDI

- Free of 2,4-isomer, which may offer unique properties
- Comparable reaction activity, can be adjusted through temperature or catalyst
- Outstanding anti-yellowing and weather resistance performance
- Excellent mechanical properties
- Pre-marketing feedback has been very positive





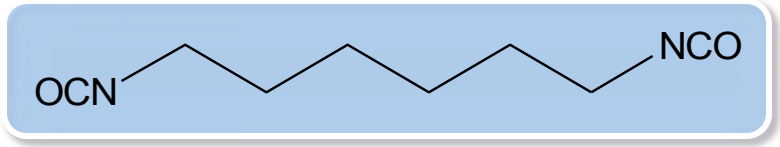


Wannate HDI

WANHUA

Yantai Wanhua Polyurethanes Co., Ltd

Wannate HDI



Hexamethylene diisocyanate

Abbr.: HDI

Molecular Formula: $C_8H_{12}N_2O_2$

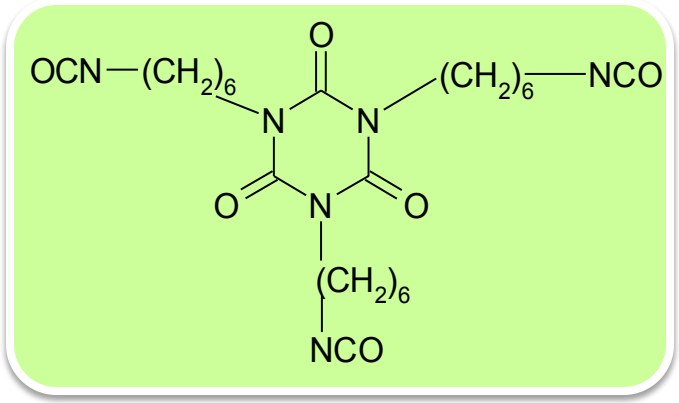
Molecular Weight: 168

Equivalent Weight: 84

NCO Content: 50%

Isomer Type: 1

Wannate HDI Trimer



More than 90% is used in the form of adducts

HDI Trimer: low viscosity, high performance, main adduct form

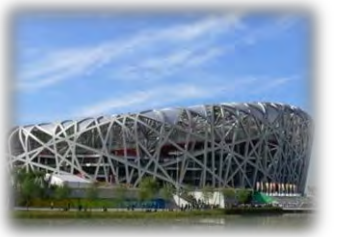
Average M_w: ≈ 500

Viscosity: ≈ 3000 mPa.s (23 ℃)

Application of Wannate HDI & Adducts

- **Automotive/aircraft refinishing and OEM coatings**
- **Anticorrosion coatings**
- **Furniture coatings**
- **Coil coatings**
- **PU adhesive & sealant**






Production Status of Wannate HDI

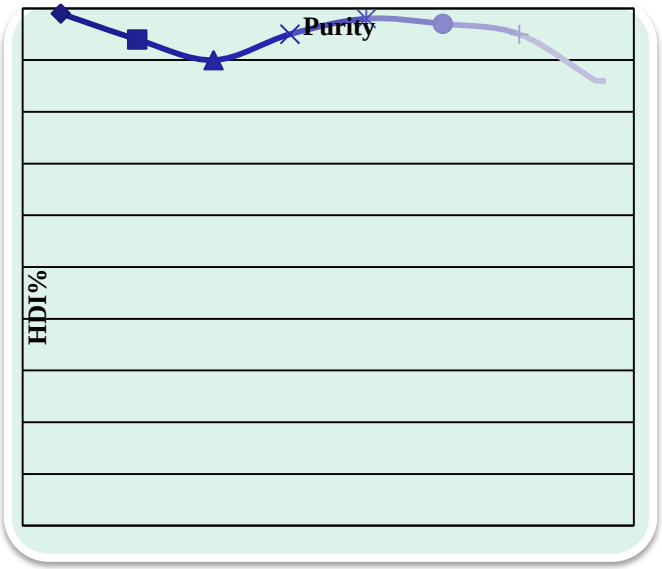
- HDI capacity in Ningbo is 20000 t/year
- Started-up in March, 2012, now running stable
- HDI trimer capacity in Ningbo is 6000 t/year
- HDI trimer will be supplied in August, 2012

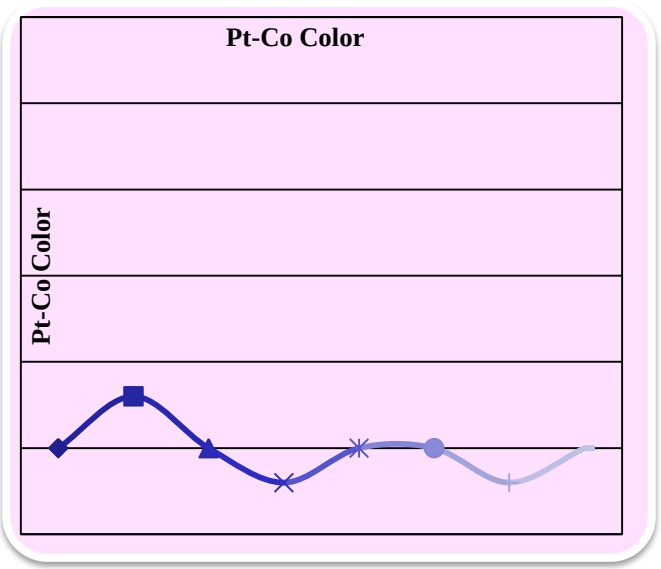
Wannate HDI VS. Competitors

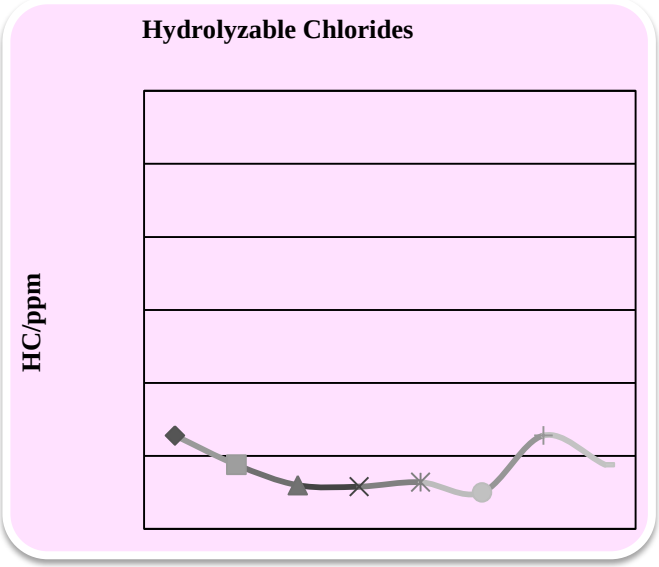
	Wannate HDI	Comp. A	Comp. B	Comp. C
Purity/%	≥ 99.50	≥ 99.50	≥ 99.50	≥ 99.50
NCO/%	≥ 49.70	≥ 49.70	≈ 50	≥ 49.70
Color (Pt-Co)	≤ 30	≤ 30	≤ 15	---
Hydrolyzable chlorides/ppm	≤ 300	≤ 100	≤ 350	≤ 300
Total chlorides/ppm	≤ 800	≤ 800	≤ 1000	---

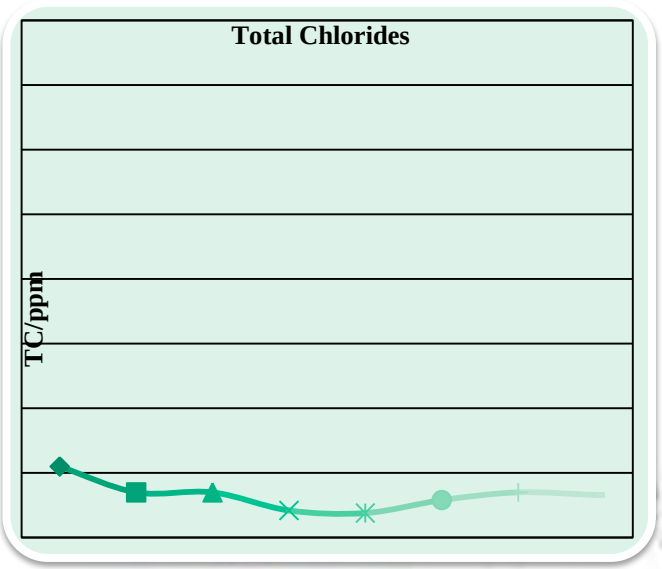
Wannate HDI shows comparable specification values to competitors

Quality Control of Wannate HDI









Thanks For Your Attention!

Crystallization Property of Wannate HMDI

trans, trans	14 ℃	12 ℃	10 ℃	9 ℃	4 ℃	0 ℃	−5 ℃
14.0%	NO 8 h	NO 8 h	NO 24 h	NO 8 h	NO 24 h	NO 24 h	NO 24 h
16.4%	NO 8 h	NO 8 h	NO 24 h	NO 8 h	NO 24 h	NO 24 h	NO 24 h
17.6%	NO 8 h	NO 8 h	NO 24 h	NO 8 h	NO 24 h	NO 24 h	YES 24 h
18.9%	NO 8 h	NO 8 h	NO 24 h	NO 8 h	YES 3 h	---	---
21.0%	NO 8 h	YES 7 h	---	---	---	---	---
22.0%	NO 8 h	YES 3 h	---	---	---	---	---

Crystallization conditions of Wannate HMDI with varying t-t isomers

Melting Property of Wannate HMDI

trans, trans	15 ℃	18 ℃	21 ℃	25 ℃	28 ℃	32 ℃
14.0%	2 h 20%	2 h 20%	2 h completely	---	---	---
16.4%	2 h 15%	2 h 15%	3h completely	---	---	---
17.6%	2 h 10%	2 h 10%	4 h completely	3 h completely	---	---
18.9%	2 h slightly	2 h slightly	4 h 70%	3 h 90%	2 h completely	2 h completely
20.0%	2 h NO	2 h NO	4 h 65%	3 h 70%	3 h completely	3 h completely
21.0%	2 h NO	2 h NO	4 h 60%	3 h 60%	3 h 95%	3 h completely

Melting conditions of Wannate HMDI with varying t-t isomers

Specifications for Wannate HDI

	Specification	Method
Purity/%	≥ 99.50	GC
NCO/%	≥ 49.70	GB 12009.4
Color (Pt-Co)	≤ 30	GB 3143
Hydrolyzable chlorides/ppm	≤ 300	GB 12009.2
Total chlorides/ppm	≤ 800	Internal