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chemicals

Excellence in polyurethane core Chemistry

Tolonate™
Easaqua™

www.vencorex.com

vencorex chemicals

Excellence in polyurethane core chemistry

• A global player

> Manufacturing sites at **Pont-de-Claix** (France) and **Freeport, TX** (USA)

> Worldwide commercial representation, partially through Perstorp's existing sales organization.

> Committed to **Safety**, **Environment** and **Sustainable Development.**

> **Solution provider** for new regulatory constraints.

> Shaped by a culture of **INNOVATION**

> Supported by **multicultural** and **international** teams

Since June 2012, Vencorex is a JV supported by PTT Global Chemical, Asia's leading integrated petrochemical company and the Perstorp Group, world leader in specialty chemicals market.

Our enterprise is recent, but our products such as Tolonate™ benefits from decades of experiences and know-how.

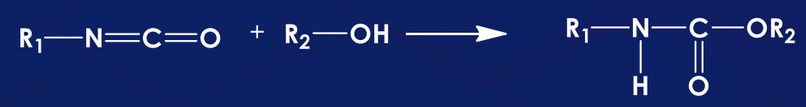
Vencorex is the owner of key technologies and a major manufacturer of aromatic (TDI) and aliphatic isocyanates, (HDI, IPDI) and their derivatives, for the polyurethane markets. With worldwide commercial representation, Vencorex has manufacturing and laboratory units in France and USA.

Let's build our future ***together!***

Introducing Polyurethane technology

Polyurethane coating technology

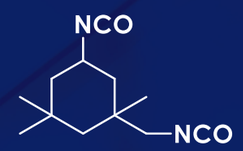
Polyurethane coatings are based on binders formed by the reaction between a (poly)isocyanate (-NCO) and another polymer containing hydroxyl groups (-OH), commonly called polyol.



The choice of raw materials, both polyols and (poly)isocyanates, is very large, enabling many combinations with a wide variety of properties. Polyurethanes based on aliphatic polyisocyanates are well-known for their outstanding properties, especially for their exceptional resistance to weathering.

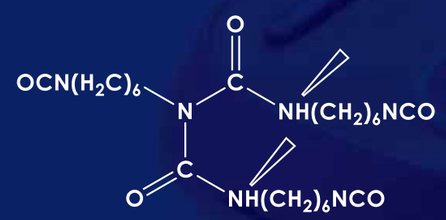
Vencorex offer is based on the 2 main aliphatic isocyanates:

Hexamethylene diisocyanate (HDI)

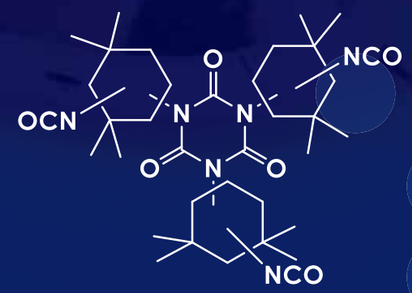


Isophorone diisocyanate (IPDI)

HDI monomer is transformed into 2 main types of «derivatives»: biuret and trimer. Both products are clear, viscous liquids, at 100% solids, soluble in organic solvents (butyl acetate, xylene, ...).



IPDI monomer is transformed in one type of "derivative": Trimer. As a solvent-free product, it is in a solid state. Commercially available at 70% solids content in solvent.



Tolonate™

Aliphatic polyisocyanates for polyurethane coatings

Our Tolonate™ isocyanates

> Outstanding appearance
> Exceptional gloss retention
> Non-yellowing upon ageing
> High-solids low VOC options
> Fast drying possibilities

The main applications where **Vencorex Tolonate™** range are ideal for polyurethane formulations are:

> Automotive primers and clearcoats (both OEM and refinish)
> Transportation coatings for buses, trucks, railway carriage and aerospace
> Marine & protective coatings
> Plastic coatings
> General industrial coatings on metal and glass
> Wood coatings
> Can & coil coatings
> Concrete coatings

Tolonate™: Leveraging the performances of polyurethane coatings

Our Tolonate™ range

Tolonate™ HDB-series
Due to internal hydrogen bonds, Tolonate™ HDBseries are more polar than the other HDI derivatives. As a result, they show:

> good compatibility with a wide range of resins (especially polyester polyols & alkyds)
> very good adhesion to a lot of substrates

Tolonate™ IDT
Due to their cyclo-aliphatic structure, Tolonate™ IDT:
> facilitate fast drying and improve initial and final hardness
> produce coatings with improved resistance to acids and solvents

Tolonate™ HDT-series
Thanks to their aliphatic nature and to their isocyanurate ring structure, Tolonate™ HDT-series show:

> exceptional UV and weathering resistance (non yellowing and very high gloss retention)
> chemical and solvent resistance
> ideal balance between high functionality and low viscosity, which explains their increasing usage in low VOC systems (high solids and solvent free formulations)

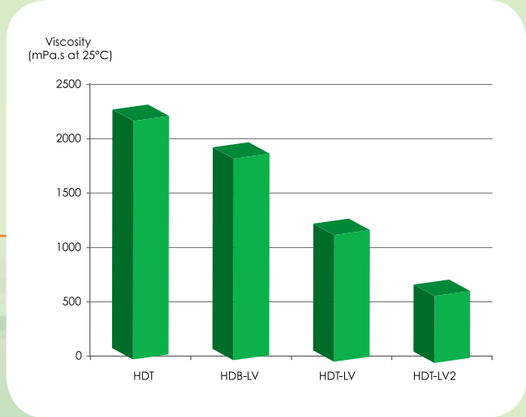
Tolonate™ key benefits

Outstanding appearance
Thanks to their high transparency and very low color, Tolonate™ polyisocyanates are ideal for producing polyurethane clearcoats and topcoats when aesthetic and durability of the coatings are critical.

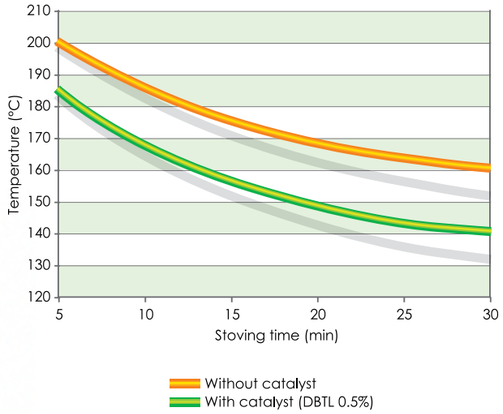
High solids low VOC options
We have implemented a special process for Tolonate™ low viscosity LV grades *(see Graph 1)*. These 100% solids products are particulary well adapted for low VOC formulations.

Exceptional gloss retention and non-yellowing properties
Polyurethane coatings with Tolonate™ show exceptional gloss retention and non-yellowing properties upon ageing.

Fast drying possibilities
We offer special grades, like the Tolonate™ IDT, Tolonate™ X FD 90 , which reduce the drying time of coatings, improving painting productivity.



Graph 1: Viscosity of 100% solids Tolonate™ grades



Graph 2: Curing conditions of 1 K formulations with Tolonate™ D2

Formulating recommendations

1K formulations with Tolonate™ D2

Tolonate™ D2 is used as a crosslinker of one-pack heat-activated coatings (as the only crosslinker or in conjunction with aminoresins).

Since Tolonate™ D2 is temporarily blocked, these 1K formulations show no reactions to humidity and do not have a limited pot-life during application. They are ready-to-use (the end-user does not have to add prior to use a hardener in precise quantity).

Typical curing conditions are 20-40 minutes at 140-150°C (280-300°F). Higher temperatures result in shorter curing times. Therefore, 1K formulations based on Tolonate™ D2 can only be used on metal or glass substrates. Conventional catalysts of urethane formulation (Lewis acid type) can be used to reduce baking temperatures or time *(see graph 2)*.

2K formulations with other Tolonate™ grades

Except Tolonate™ D2, the other Tolonate™ grades are used as crosslinkers of two-pack (2K) polyurethane formulations. The paint applicators have two separated components. The pot containing the polyol is usually called part A, while the Tolonate™ based hardener is called part B.

Just prior to use, end-users have to mix the two parts in a specified ratio (see processing recommendations, page 10). As soon as the two packs are mixed, the NCO- groups of the polyisocyanate start to react with the OH-groups of the polyol leading to a slow, continuous and not reversible increase of viscosity. The time during which the coating can be used is called «pot-life». The end of the pot-life is usually achieved once the initial viscosity of the ready-to-use coating has doubled.

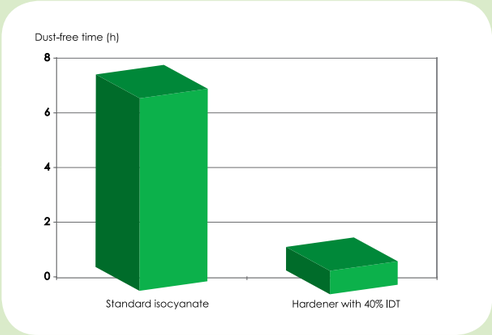
Since the NCO + OH reaction takes place at room temperature, the 2K polyurethanes are used on all the substrates which are sensitive to heat (like wood and plastics) and on all the objects which are too big to be stoved (airplanes, bridges, railway carriage, etc.).

2K polyurethane coatings are either cured at room temperature or forced dried at 50 to 80°C or even baked at 140°C, depending of the final applications and paint line equipment.

Fast drying 2K formulations

Fast drying is a key parameter to increase paint productivity and to minimize dust issues.

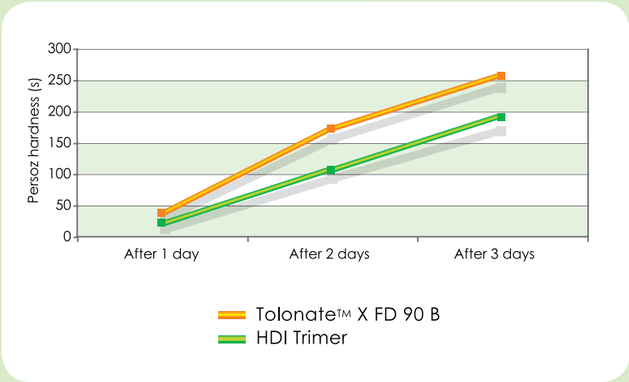
Physical drying time can be strongly reduced and the rate of hardness development increased by using Tolonate™ IDT 70 *(see Graph 3)*. In order to keep an acceptable level of coating flexibility, Tolonate™ IDT 70 shall be used in blends with Tolonate™ HDT or HDB grades.



Graph 3: effect of Tolonate™ IDT 70 on dust time

Tolonate™ X FD 90 B is a high functionality, fast drying aliphatic polyisocyanate based on HDI-trimer, supplied at 90% solids in butyl acetate.

Tolonate™ X FD 90 B gives higher hardness (up to 39%), compared to a standard HDI trimer *(see Graph 4)*.



Graph 4: clearcoat based on Synocure 852 BA 80, Application on glass panels (200 µm) – air drying (23°C – 50% HR)

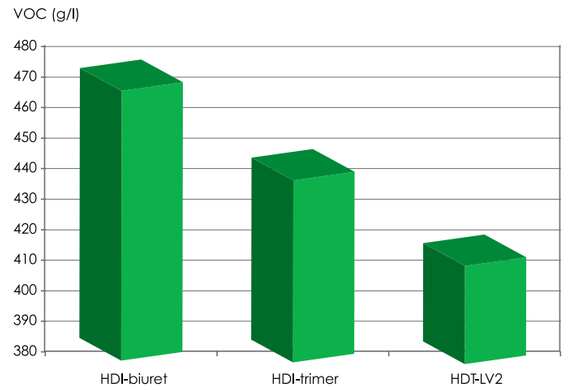
High solids, low VOC 2K formulations with Tolonate™ HDT-LV2

> In order to comply with new regulations, formulators have to offer low VOC (Volatile Organic Compounds) formulations.

> We have developed a unique process leading to low viscosity, 100% solids HDI-trimer Tolonate™ HDT-LV2.

Thanks to Tolonate™ HDT-LV2, high solids, VOC compliant coatings can be prepared *(see Graph 5)*.

These formulations show similar properties to the ones based on standard polyisocyanates.



Graph 5: comparison of VOC level of clearcoats on various hardeners

Processing recommendations

NCO/OH ratio: calculation and impact on final properties

Polyurethane network is created by the reaction between the Tolonate™ – based hardener and the polyol. In theory a stoichiometrical ratio should be used (NCO/OH = 1), i.e. an equal number of NCO-groups of Tolonate™ will have to react with the OH-groups of the polyol*.

> But in practice the NCO/OH ratio varies, depending of the required end properties.

In the case of primer coats – NCO/OH is usually lower than 1 (0.7 to 0.9 for example), to obtain a better film flexibility and a better inter-coat adhesion with the topcoat.

In the case of topcoats – NCO/OH is usually higher than 1 (1.1 to 1.5 for example) in order to ensure a perfect crosslinking of the film, and thus durability and protection against UV light, humidity and chemicals.

> An easy way to calculate the quantities of each component (Tolonate™ and polyol) is obtained by using the so called "equivalent weights". They are either indicated on the product technical data sheets or can be calculated from the NCO content (%) and OH content (%), as explained here after:

Tolonate™

EW_{NCO} = equivalent weight of NCO in grams = 42x100/(% NCO)

Polyol

EW_{OH} = equivalent weight of OH in grams = 17x100/(% OH)

Technical data sheets of polyols sometimes only mention the OH index (I_{OH} in mg KOH per gram of dry resin). OH content (%) can be calculated from this using the following formula:

% OH = I_{OH} / 32.94

> The ratio between the two components can then be obtained by using:
- quantity of Tolonate™ (in grams) = NCO/OH x EW_{NCO} (as supplied)
- quantity of polyol (in grams) = EW_{OH} (as supplied) = EW_{OH} (on solids) / (solids content)

> Example:
For a polyol with an OH% = 4% (on solids) and a solids content of 60% by weight:

EW_{OH} (on solids) = 17x100/4 = 425g
EW_{OH} (on delivery form) = 425/(60/100) = 708g

Quantity of Tolonate™ HDB 75 MX to be used to have NCO/OH = 1.1:
As NCO% = 16.5% then EW_{NCO} (as supplied) = 42 x 100/16.5 = 255g

We therefore need 255 x 1.1 = 280g of Tolonate™ HDB 75 MX for 708g of polyol, which means 39.6g of Tolonate™HDB 75 MX for 100g of polyol.

**** Formulators have to make their own tests in order to define the best NCO/OH ratio depending of their formulation and final application.***

Dilutions of Tolonate™ with solvents in 2K formulations

In order to reduce the viscosity of Tolonate™ and obtain simple mixing ratio between part A and part B, formulators usually dilute Tolonate™ using one or more solvents.

Type of solvent(s)

Some of the most common solvents of the paint industry can be used to dilute Tolonate™, with the exception of those that may react with the polyisocyanate, such as alcohol or glycol monoethers. Besides, Tolonate™ are not fully soluble in aliphatic hydrocarbons (like White Spirit), which should not be used.

The best solvents for Tolonate™ are esters (like butyl acetate) and ketones (like MIBK: methyl isobutyl ketone). Ether esters (like MPA: methoxy propyl acetate) and aromatic hydrocarbons (such as xylene or naphta solvents) are also commonly used. Dilutions using hydrophilic solvents, such as ketones, are more sensitive to atmospheric humidity than those produced with hydrophobic solvents such as aromatic hydrocarbons.

Water content of the solvent(s) and impurities reacting with NCO

Like all isocyanates, Tolonate™ react with water. It is therefore essential to use solvents with a water content lower than 500 ppm (preferably lower than 300 ppm), which are referred to as "urethane grade solvents."

We also recommend to carefully check the quantity of impurities likely to react with NCO groups, such as butanol and/or acetic acid in butyl acetate.

Dilution level

It is theoretically possible to dilute Tolonate™ to a high degree. However, the higher the quantity of solvent, the greater the risk that traces of water from the solvent may cause problem with the diluted polyisocyanate.

That is why it is recommended to go no lower than 35-40% solids by weight. Below this level, there is a higher risk of obtaining turbidity, precipitates and even gels.

It should be noted that trimers can generally withstand higher dilution levels than biurets.

Product data summary

	Tolonate™	Colour (1)	Viscosity Avg. mPa.s(2)	NCO Avg. %(3)	Free Monomer %	Solid content Avg. %	Solvent type	Bulk density kg/m3(2)	Flash point °C(4)	Equivalent Weight g(3)	Refractive index(2)
HDI Derivatives	**Biurets – Polyesters Compatibility**										
	Standard grades										
	HDB	≤ 40	9000	22	< 0.3	100	-	1120	> 120	191	1.505
	HDB 75 B	≤ 40	150	16.5	< 0.3	75	B	1150	35	255	1.4747
	HDB 75 M	≤ 40	250	16.5	< 0.3	75	M	1083	55	255	1.4761
	HDB 75 MX	≤ 40	250	16.5	< 0.3	75	MX	1067	38	255	1.4894
	Low viscosity										
	HDB-LV	≤ 40	2000	23.5	< 0.3	100	-	1120	> 120	179	1.5013
	Trimers – Durability										
	Standard grades										
	HDT	≤ 40	2400	22	< 0.2	100	-	1160	> 120	191	1.5039
	HDT 90	≤ 40	500	19.8	< 0.2	90	SB	1120	53	212	1.4988
	HDT 90 B	≤ 40	450	20	< 0.2	90	B	1132	48	210	1.4923
	Fast drying										
	X FD 90 B	≤ 60	2000	17.4	< 0.5	90	B	1130	48	240	1.4960 (5)
	Low viscosity										
	HDT-LV	≤ 40	1200	23	< 0.2	100	-	1160	> 120	183	1.5004
	HDT-LV2	≤ 40	600	23	< 0.5	100	-	1131	> 120	183	1.4986
	For thermosetting formulation (NCO-Blocked)										
	D2	≤ 40	3250	11.2	-	75	S	1060	49	370	1.5103
IPDI Derivatives	IDT 70 B	≤ 60	600	12.3	< 0.5	70	B	1060	29	342	1.48

B = butyl acetate X = xylene M = methoxpropyl acetate S = aromatic hydrocarbon NM = not measured
(1) = Hazen or APHA (2) = at 25°C (3) = on delivery form (4) = in closed cup

Influence of temperature on viscosity

	Tolonate™	Viscosity (mPa.s) at various temperatures						
		-20°C	-10°C	0°C	10°C	20°C	40°C	60°C
HDI Derivatives	**Biurets**							
	Standard grades							
	HDB	NM	NM	241470	66310	22730	3540	860
	HDB 75 B	4440	1810	800	390	210	80	35
	HDB 75 M	NM	NM	1450	600	310	110	45
	HDB 75 MX	11000	3850	1820	700	340	110	50
	Low viscosity							
	HDB-LV	NM	65680	19660	7190	2910	665	200
	Trimers							
	Standard grades							
	HDT	NM	75400	26680	8530	3410	770	250
	HDT 90	27430	9070	3420	1440	690	200	80
	HDT 90 B	NM	NM	2700	1090	570	180	75
	Fast drying							
	X FD 90 B*	NM	36700	12550	6470	2950	1470	NM
	Low viscosity							
	HDT-LV	NM	27400	9380	3810	1640	410	140
	HDT-LV2	NM	15580	5170	2180	1000	280	105
	Blocked							
	D2	NM	NM	10100	24060	6370	960	250
IPDI Derivatives	IDT 70 B	NM	NM	NM	2320	820	160	76

Easaqua™

Polyisocyanates for easy waterborne polyurethane coatings

Our Easaqua™ product line has been specifically designed for waterborne polyurethane formulations to meet the growing need for easy-to-use and environmentally-friendly coatings.
As formulation requirements have evolved, so has our line of products, which includes several new additions offering faster drying, lower viscosity and improved humidity resistance.

Our Easaqua™ aliphatic polyisocyanates

> Enable easy mixing and fast drying

> Meet demands for environmentally friendly performance

> Deliver innovative technology with broad compatibility

> Include ready-to-use grades

The main applications where our **Easaqua™** range is ideal for water-borne polyurethane formulations are:

> Wood coatings

> Plastic coatings (including soft-feel formulations)

> Coatings for automotive repair, transportation and agricultural equipment

> Metal coatings for general industry

> Concrete coatings

Our Easaqua™ range
Self-emulsifiable polyisocyanates

- Easaqua™ WT 2102
- Easaqua™ M 501
- Easaqua™ M 502
- Easaqua™ X D 401
- Easaqua™ X D 803
- Easaqua™ X L 600

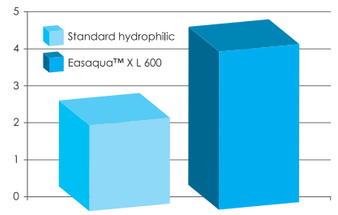
New Easaqua™ X L 600:
Easy dispersibility with improved humidity resistance

Our latest innovation, **Easaqua™ X L 600**, has been specifically designed to meet your highest demands for humidity resistance combined with the same easy mixing that our Easaqua™ range is widely appreciated for. Easaqua™ X L 600 shows a very narrow particle size distribution after emulsification into waterborne media.

Thanks to its lower hydrophilicity it also provides high resistance to moisture, offering greater protection of the substrate that the final coating is applied to.

In addition, Easaqua™ X L 600 has one of the lowest viscosities of all the products in the Easaqua™ range and thus has a reduced need for solvent (it can even be used without any solvent at all). Easaqua™ X L 600 shows a very interesting balance between viscosity and NCO content.

Improved adhesion on metal
A 2K waterborne polyurethane topcoat based on the new Easaqua™ X L 600 shows better adhesion after immersion into water at 40 °C for ten days, compared to standard hydrophilic polyisocyanate *(see graph 1).*



White topcoat, applied over a commercial primer, quotation of crosshatch cut test from 0 to 5 where 5 is best

Graph 1: new Easaqua™ X L 600 provides excellent adhesion on metal, even after immersion into hot water.

FOCUS ON INNOVATION

The latest development in our Easaqua™ range, Easaqua™ X L 600, is an innovatively modified polyisocyanate that:

> *Combines easy dispersibility and improved humidity resistance*

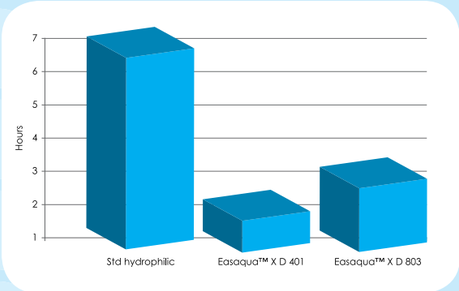
> *Ensures very narrow particle size distribution after emulsification into water*

> *Achieves the best balance between low viscosity and functionality*

> *Improves adhesion onto a wide range of substrates*

Easy waterborne solutions for coating applications

Easaqua™ polyisocyanates are ideal for formulating waterborne high-performance polyurethane coatings.



Graph 2: dust free time 25% to 60% shorter with Easaqua™ X D 401 and X D 803 in comparison with standards grades.

Hydrophilically modified polyisocyanates

All our Easaqua™ grades are hydrophilically modified polyisocyanates and self-emulsifiable into water.

They are used as cross-linkers of two-pack (2K) formulations, where they contribute to excellent miscibility, fast drying, high gloss, outstanding durability and excellent chemical resistance of the polyurethane film.

***Picture 1.* Self-emulsification of Easaqua™**
Shows hand mixing of Easaqua™ (right) and standard hydrophobic isocyanate (left)

Easy mixing

No high speed mixing equipment is required. Easaqua™ products are self-emulsifying and very easy to incorporate into waterborne coating formulations.

Hand mixing is sufficient:
Easaqua™ grades do not require high-shear or high-speed special equipment *(see picture 1).*

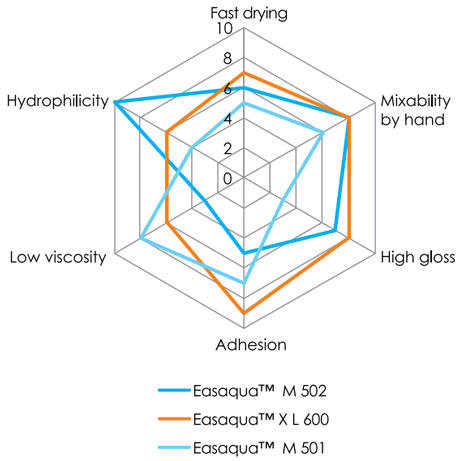
***Picture 2.* Wood panels after stackability test**
Shows contact between coated panels under 1200 kg/m2 for 16 hours with Easaqua™ X D 401 (left) and with a standard hydrophilic hardener (right)

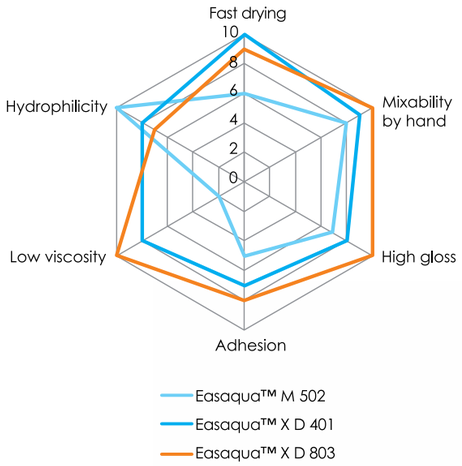
Fast drying

Better hardness and thus, improved stackability. Coatings based on Easaqua™ X D 401 and X D 803 show a dust free time 25% to 60% shorter, resulting in higher efficiency in terms of application process and less film defects *(see graph 2).*

Easaqua™ X D 401 also gives improved stackability of the coated panels *(see picture 2).*

Key properties





Ultra low Voc & APEO-free options

Easaqua™ products are the environmentally-responsible choice for high performing, ultra low VOC and APEO-free coating formulations. Our products support sustainable development and meet the ever-increasing environmental protection regulations around the world.

Worldwide registered

All Easaqua™ products are designed to meet global regulations and are registered in the following inventories:

> EINECS (Europe)
> TSCA (USA) and DSL (Canada)
> ENCS (Japan, MITI agency), ECL (South Korea)
> AICS (Australia) and IECS (China)

Wide compatibility with most polyols

Easaqua™ products are compatible with most waterborne polyols (acrylics, polyesters, PUDs etc.), maximizing your options for formulating primers, clearcoats and pigmented topcoats, while minimizing costs.

The prime solution for 2K waterborne systems

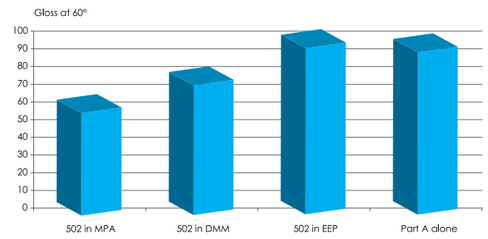
2K formulations with self-emulsifiable Easaqua™

NCO/OH ratio: In most cases an NCO/OH ratio between 1.0 and 1.4 is used. If the ratio is too high, this may reduce pot-life and film defects such as foams and haze may occur. If the ratio is too low, this may lead to lower hardness and poorer chemical resistance. In the case of non-hydroxylated PUDs, the quantity of Easaqua™ to be added is empirically determined.

Blending Easaqua™ with other polyisocyanates:

It is generally recommended to use one grade of Easaqua™ as the only cross-linker. However, self-emulsifiable Easaqua™ is fully compatible with hydrophobic Tolonate™ and it is possible to make blends in order to obtain a wide range of properties. Low viscosity HDI trimers, Tolonate™ HDT-LV and Tolonate™ HDT-LV2 are the most widely used grades in conjunction with Easaqua™.

Dispersibility properties: When the solvent used to dilute an Easaqua™ grade is properly selected, very small particles and very narrow distribution are obtained after emulsification in water. The solvent type and quantity used to dilute the Easaqua™ based cross-linker will influence film properties, such as gloss*(see table 1).*



Graph 3: Gloss of 2K waterborne clearcoat for parquet: comparison of cross-linkers based on Easaqua™ M 502 diluted with 30% of various solvents.

Depending of the type and quantity of solvents used to dilute Easaqua™ products, quality of the self-emulsification varies.

Dilutions of Easaqua™ with solvents: Adding organic co-solvents to Easaqua™ polyisocyanates is usually not necessary, but it can help incorporate the hardener into very low viscous formulations, such as clearcoats, and improve optical properties of the film. Solvents containing -OH groups (alcohols, water, etc) must not be used *(see graph 3).*

PRODUCT DATA SUMMARY	Viscosity* (mPa.s at 25 °C)	NCO* (%)	Solids content* (%)	APEO-free (1)
Self-emulsifiable polyisocyanates				
Easaqua™ WT 2102	4,300	19.0	100	No
Easaqua™ M 501	1,100	21.6	100	Yes
Easaqua™ M 502	3,600	18.3	100	Yes
Easaqua™ X D 401	1,050	15.8	85	Yes
Easaqua™ X D 803	200	12.2	69	Yes
Easaqua™ X L 600	1,500	20.6	100	Yes
Hydrophobic polyisocyanates				
Tolonate™ HDT-LV	1,200	23.0	100	NA
Tolonate™ HDT-LV2	600	23.0	100	NA

** average value ** blocked NCO*
(1) APEO-free: without any alkyl phenol ethoxylate NA: not applicable

Easaqua™/solvent (wgt)	Butyl acetate	Shellsoll A	MPA	PGDA	DIB	DMM	EEP	BGA	BGDA	NMP
Easaqua™ WT 2102										
80/20	5	5	5	5	5	1	5	5	5	1
70/30	5	1	4	5	4	NM	5	5	5	NM
Easaqua™ M 502										
90/10	5	5	5	5	5	5	5	5	5	4
70/30	1	1	5	5	1	5	5	5	5	4
Easaqua™ X D 401										
88/12	5	1	5	5	4	5	5	5	5	5

Table 1: reactions of Easaqua™ in solvents

Rating from 5: excellent to 0: not self-emulsifiable - NM: not measured - MPA: Methoxy Propyl Acetate PGDA: Propylene Glycol DiAcetate DIB: Diisobutyl Esters DMM: Di Methyl Di Propylene Glycol EEP: Ethyl 3-EthoxyPropionate BGA: Butyl Ethylene Glycol Acetate BGDA: Butyl Diethylene Glycol Acetate NMP: N-Methyl Pyrrolidone

Safety instructions

Formulating Easaqua™ and Tolonate™ in waterborne systems is not hazardous but requires following a few simple instructions:

> Never add water to the hardener, but always pour Easaqua™ into the aqueous coating containing the polyol resin

> Never keep the ready-to-use coating hermetically sealed once the mixture (polyol + hardener) has been made

> Never put the waste into a hermetically sealed collecting tank; use a tank equipped with a safety valve to enable the release of gases

> Before any modification of the hardener, previous lab tests need to be run on small quantities

Vencorex chemicals



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your core partner in polyurethane chemistry

Vencorex is the owner of key technologies and a major manufacturer of aromatic (TDI) and aliphatic isocyanates, (HDI, IPDI) and their derivatives, for the polyurethane markets. Relying on a worldwide commercial representation, Vencorex has manufacturing and lab units in France and USA. Vencorex is supported by PTT Global Chemical, Asia's leading integrated petrochemical company and the Perstorp Group, a world leader in specialty chemicals market.

Let's build our future ***together!***

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