Introduction of Blocked carboxylic acid

Blocked carboxylic acid is a compound with a latent carboxyl group.

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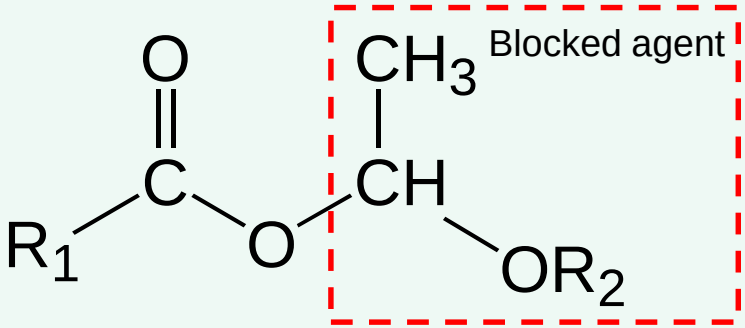
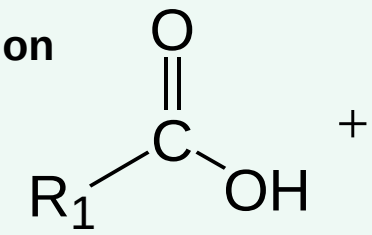
Outline of Blocked carboxylic acid

About Blocked carboxylic acid

- Compound which generates carboxylic acid by thermal dissociation of blocked agent



Dissociation by heat



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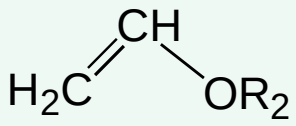


Blocked carboxylic acid (Hemiacetal ester)

Carboxylic acid

Blocked agent

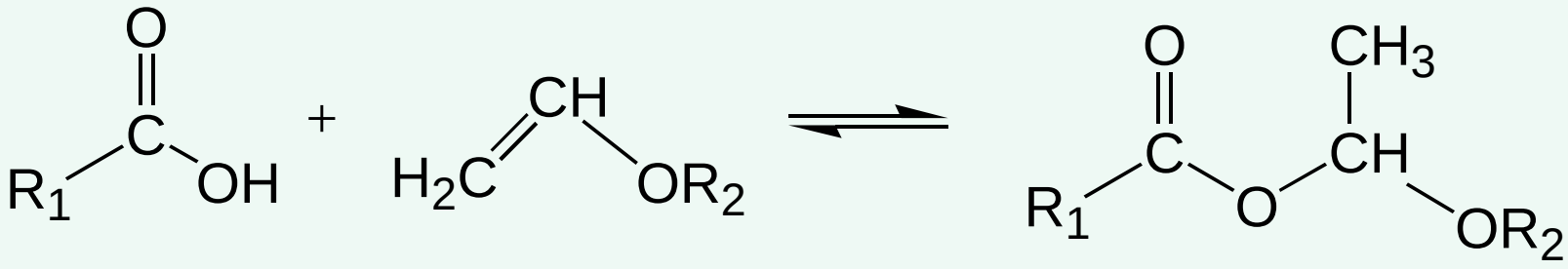
Features of Blocked carboxylic acid

- Highly active carboxyl groups can be temporarily inactivated.
- It is a liquid compound with high solubility and compatibility to organic solvents and epoxy resin.
- Regeneration of carboxylic acid can be controlled by the choice of carboxylic acid and the blocked agent.

Features of Blocked carboxylic acid -1 ～Inactivation～

Blocked carboxylic acid can temporarily inactivate the active carboxyl groups.

Carboxylic acid　Blocked agent　Blocked carboxylic acid

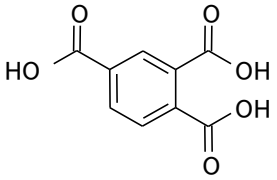
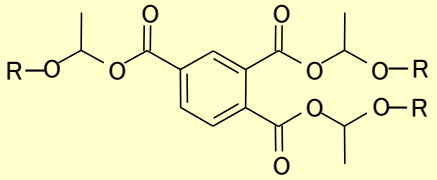


Active　Inactive

Advantages of this feature

- Blocked carboxylic acid is very useful as a latent hardener for epoxy resin compositions.
- Epoxy resin composition using blocked carboxylic acid has excellent storage stability.

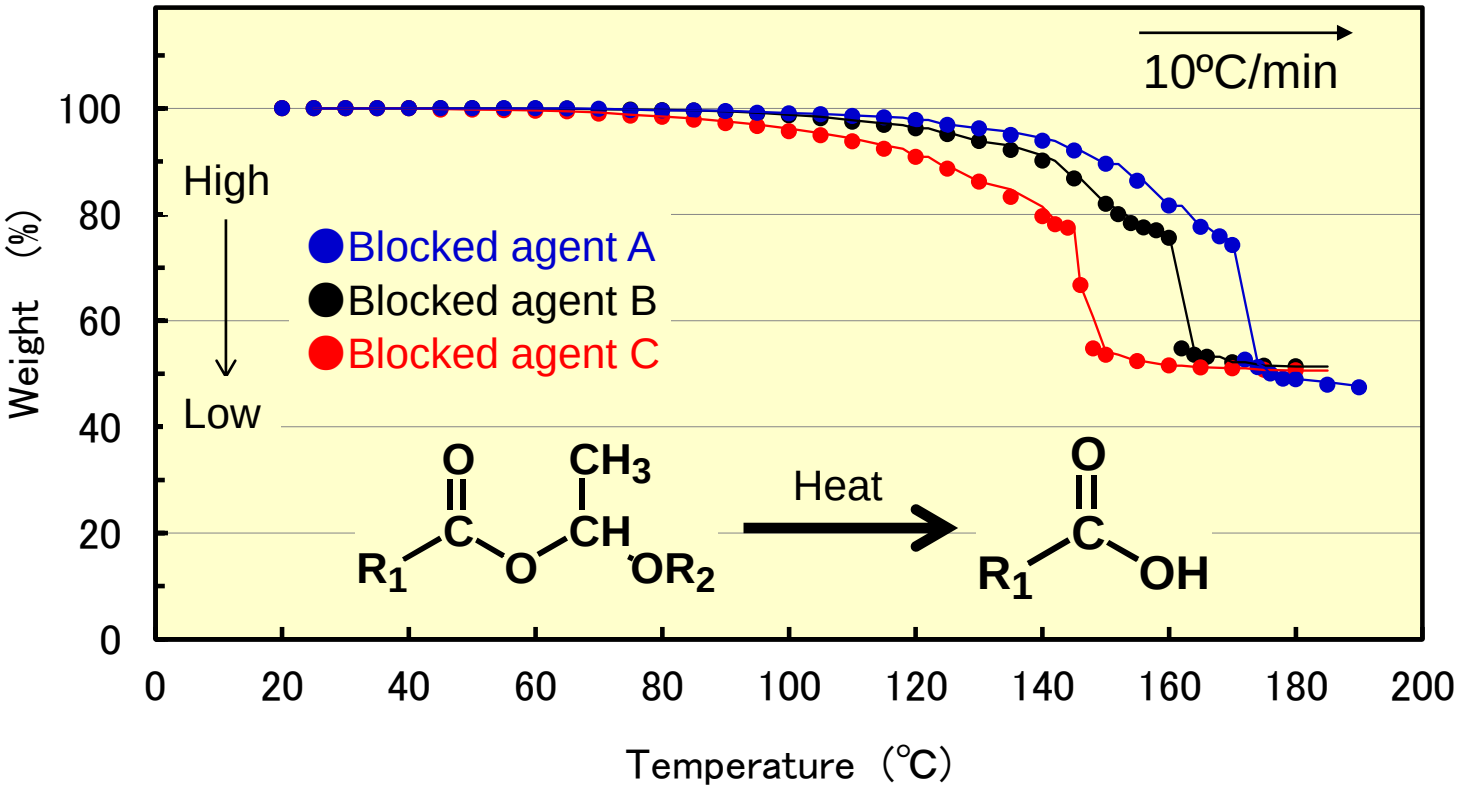
Features of Blocked carboxylic acid -2 ～Solubility～

Item	Carboxylic acid (1,2,4-Trimellitic acid)	Blocked carboxylic acid (Blocked1,2,4-Trimellitic acid)
Structure		
Appearance	Powder 	Transparent liquid 
Solubility, Compatibility	Low (Hard to dissolve)	High (Easy to dissolve)

Item	Solubility and compatibility (50wt%)				
	n-Hexane (SP=7.27)	MIBK (SP=8.58)	Butyl acetate (SP=8.69)	Benzene (SP=9.16)	Bisphenol A diglycidyl ether
Carboxylic acid (1,2,4-Trimellitic acid)	**Insoluble**	**Insoluble**	**Insoluble**	**Insoluble**	**Insoluble**
Blocked carboxylic acid	**Soluble**	**Soluble**	**Soluble**	**Soluble**	**Soluble**

Features of Blocked carboxylic acid -3 ～Regeneration～

Regeneration behavior of carboxyl group in Blocked carboxylic Acid
- Carboxylic acid：1, 2, 4-Trimellitic acid
- Blocked agent：3 types in different structure（A, B, C）



Dissociation temperature can be controlled by the choice of the blocked agent.

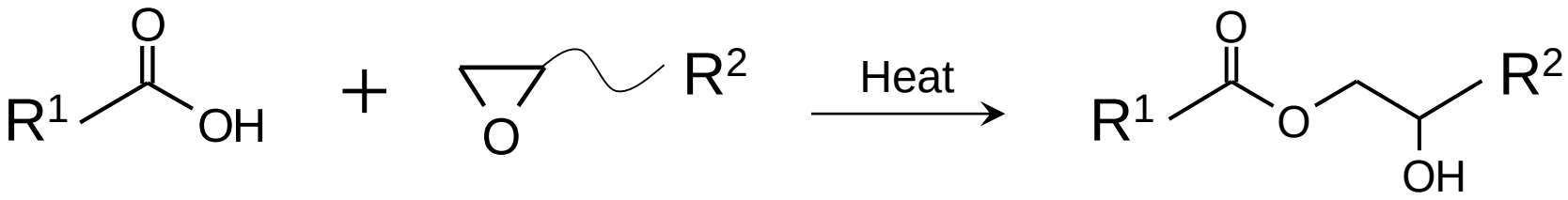
Use as a latent hardener for epoxy resin composition

Item	Carboxylic acid/ Epoxy curing system	Blocked carboxylic acid/ Epoxy curing system
Advantage	• Good cured film property (Thermal stability, Transmittance, Chemical resistance, Light resistance, Adhesion, etc)	• Good cured film property (Thermal stability, Transmittance, Chemical resistance, Light resistance, Adhesion, etc) • Excellent storage stability (One component type possible) • High solid composition possible • High latitude in formulation • High cross-linked cured film can be obtained
Weak point	• Poor storage stability (Two component recommended) • Not suitable for high solid composition • Low latitude in formulation	• Not suitable for thick film application (Appearance of Void) • Not suitable for water-based composition

The weak point resolves by applying Blocked carboxylic acid.
Cured film property improves by adding hardener in large amount.

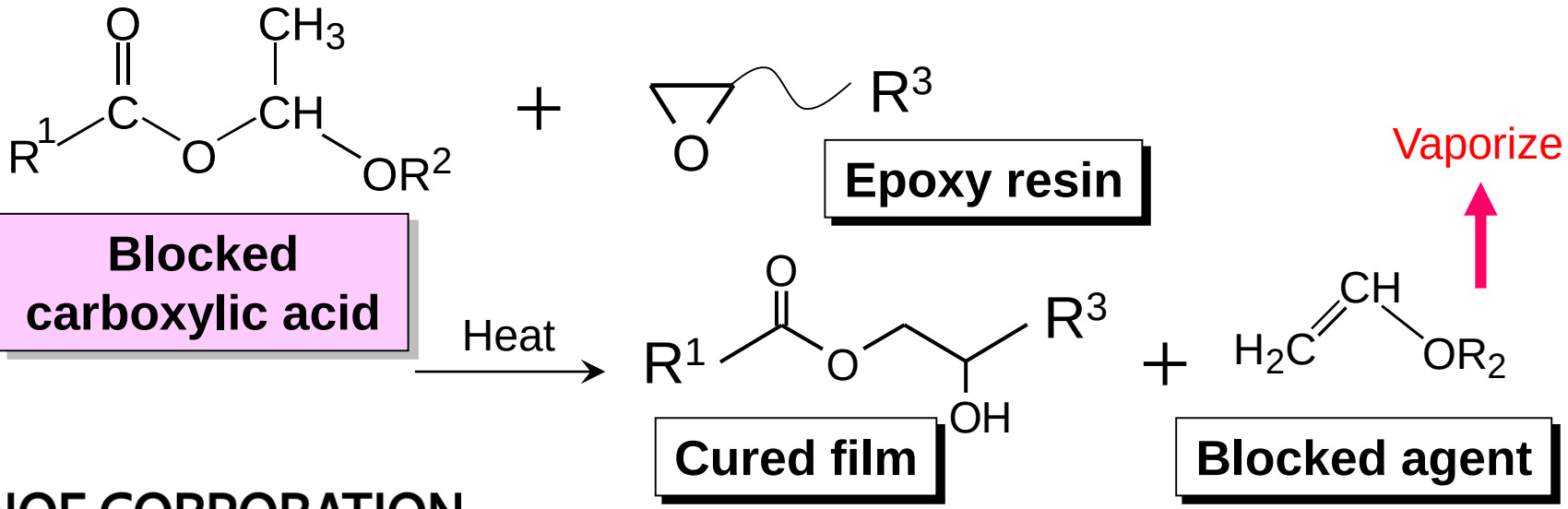
Scheme of Blocked carboxylic acid/Epoxy curing system

Carboxylic acid/Epoxy curing system

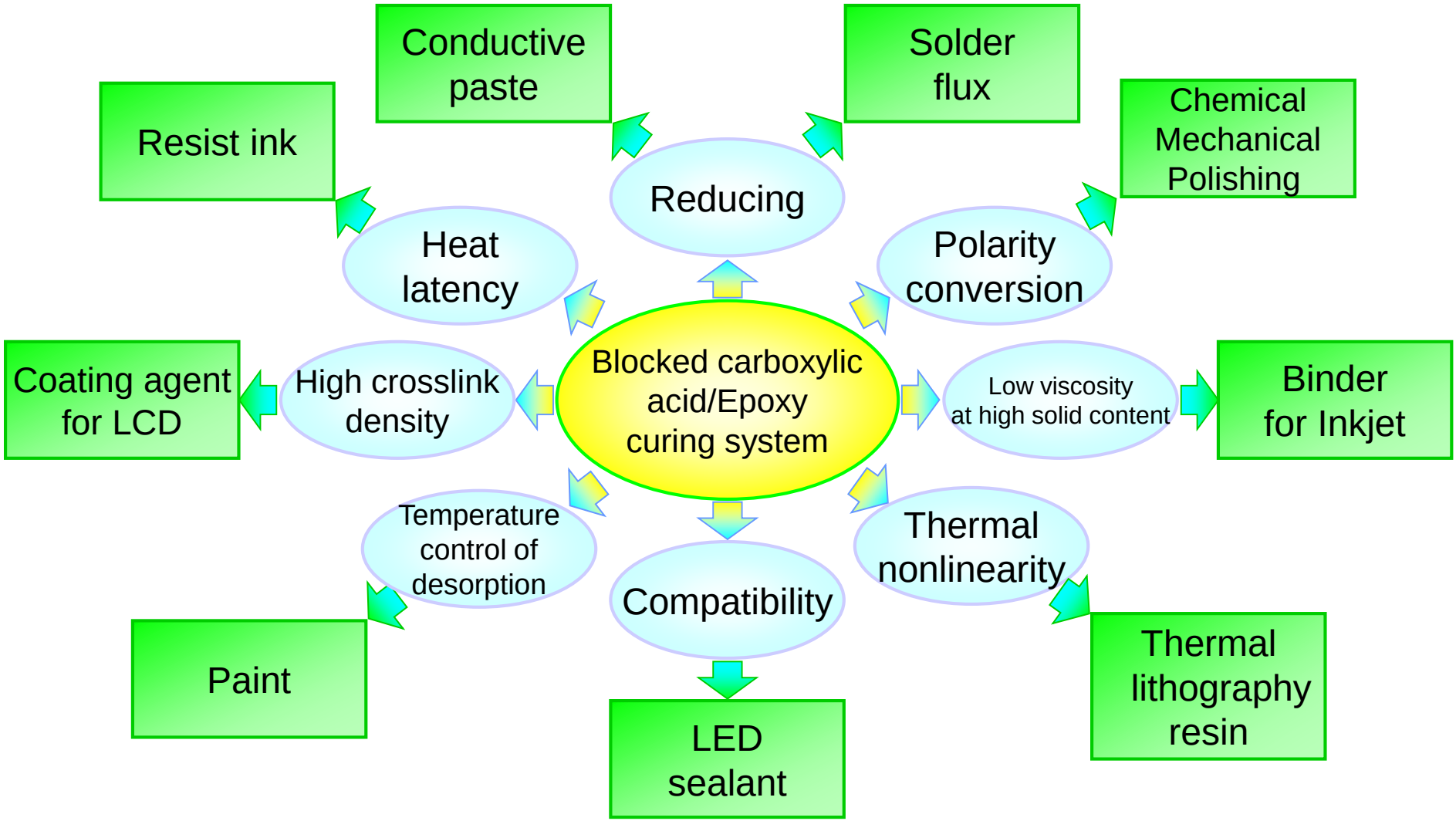


Carboxylic acid **Epoxy resin** **Cured film**

Blocked carboxylic acid/Epoxy curing system



Application example of Blocked carboxylic acid technology



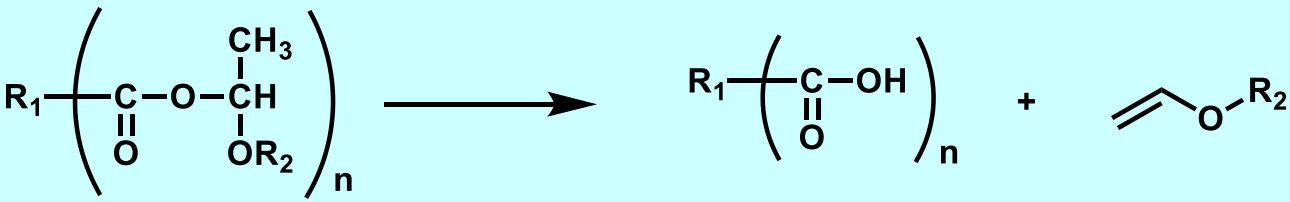
Blocked carboxylic acid ～Product list～

Product name	Carboxylic acid	Type of Blocked agent	Type of Blocked carboxylic acid[1)]
NOFCURE™ TN-1	1, 2, 4-Trimellitic acid	Mono-alkyl	Type A
NOFCURE™ TN-2	Aliphatic modified carboxylic acid	Mono-alkyl	Type A
NOFCURE™ TN-5	1, 2, 4-Trimellitic acid	Mono-alkyl	Type A
NOFCURE™ TN-6	1, 2, 4, 5-Pyromellitic acid	Mono-alkyl	Type A
SANTACID™ D-2	Aliphatic modified carboxylic acid	Di-alkyl	Type B
SANTACID™ G	Glutaric acid	Di-alkyl	Type B

1） Type A: Addition reaction of polyhydric carboxylic acid and alkyl vinyl ether
Type B: Polyaddition reaction of dicarboxylic acid and divinyl ether

Type of Blocked carboxylic acid

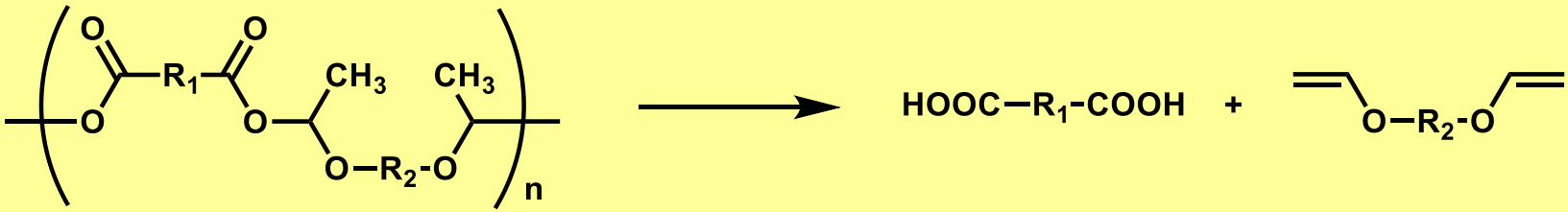
A type：Polyhydric carboxylic acid and alkyl vinyl ether



Features

- Generates polyfunctional carboxylic acid. High cross-linked cured film can be obtained when combined with epoxy resin.
- Recommended application; Coating agent

B type：Dicarboxylic acid and divinyl ether



Features

- Generates bifunctional carboxylic acid. Oxides on metal surface can be removed with the generated carboxylic acid.
- Recommended application; Solder flux, Conductive paste, Sealant

Blocked carboxylic acid ～Property～

Product name	Carboxylic acid	Active ingredient (wt%)	solvent	Viscosity[3] (mPa･s)	Acid equivalent[4] (g/mol)	Dissociation temperature (℃)
NOFCURE™ TN-1	1, 2, 4-Trimellitic acid	60	PGMEA[1]	7	260	134
NOFCURE™ TN-2	Aliphatic modified carboxylic acid	67	Aromatic hydrocarbon	30	420	>170
NOFCURE™ TN-5	1, 2, 4-Trimellitic acid	60	PGMEA[1]	6	260	129
NOFCURE™ TN-6	1, 2, 4, 5-Pyromellitic acid	60	PGMEA[1]	7	250	117
SANTACID™ D-2	Aliphatic modified carboxylic acid	77	Butyl diglyme[2] Divinyl ether	17,000	385	208
SANTACID™ G	Glutaric acid	91	Divinyl ether	4,000	150	221

1) 2-Acetoxy-1-methoxy propane (CAS registry number：108-65-6, Boiling point：146 ℃)
2) Diethylene glycol dibutyl ether (CAS registry number：112-73-2, Boiling point： 256 ℃)
3) Measurement temperature : 25 ℃
4) Acid equivalent is the product's value.(Including solvent)

Numerical values are typical values and are not guaranteed as standard values.

Blocked carboxylic acid ～Regulatory information～

Product name	ENCS (JAPAN)	KECL (Korea)	IECS (China)	NECSI (Taiwan)	EINECS (EU)
NOFCURE™ TN-1	Registered	Registered	Registered	Registered	Unregistered
NOFCURE™ TN-2	Registered (Maximum 10 t/year)	Unregistered	Unregistered	Registered	Unregistered
NOFCURE™ TN-5	Registered	Unregistered	Registered (Maximum 9.99 t/year)	Registered	Unregistered
NOFCURE™ TN-6	Registered (Maximum 1 t/year)	Unregistered	Unregistered	Unregistered	Unregistered
SANTACID™ D-2	Registered (Maximum 1 t/year)	Unregistered	Unregistered	Registered	Unregistered
SANTACID™ G	Registered (Maximum 1 t/year)	Unregistered	Unregistered	Registered	Unregistered

*If you have any request for a registration of unregistered blocked carboxylic acid, please let us know.

Precautions for designing coating agents

- Blocked carboxylic acid can not be used for water-based coating agent because the dissociation of block agent will be promoted.
- Coating agent which contains solvent with hydroxyl group (alcohol etc.), reaction accelerator and other acid substances may promote dissociation of block agent. Therefore, please determine the use of coating agent after the confirmation of its storage stability(viscosity change) .
- NOFCURE products have high flammability. Therefore, it needs to be kept away from heat, sparks, flames and static electricity. For further details, please refer to the SDS of each product.