

Ethyleneimine Polymer for cross bridge of creation

# EPOMIN POLYMENT

For more detailed information, please contact to Coating Materials Business Unit of Performance Chemical Business Div.(Tokyo, Osaka)

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# EPOMIN POLYMENT

# Introduction

Ethyleneimine (EI) has high reactivity, and it is used and well known as pharmaceutical intermediate product and / or raw material of amine polymer.

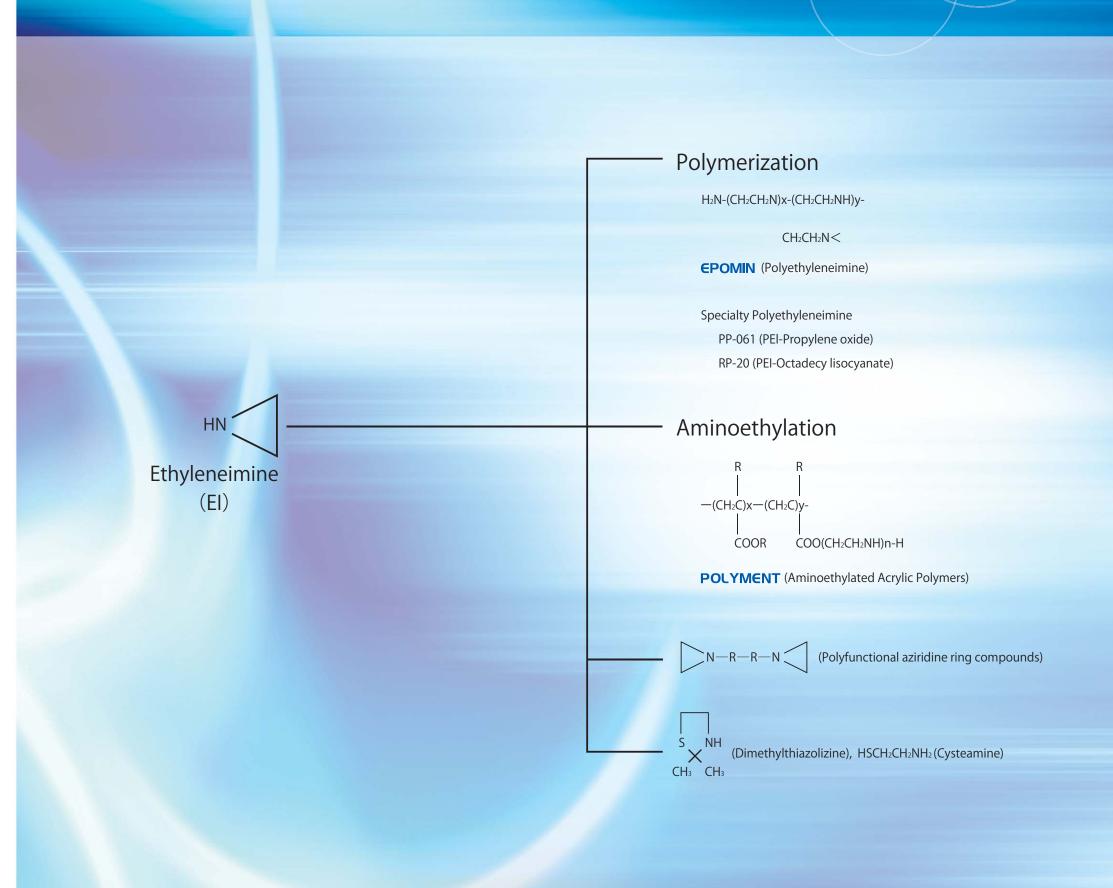
Since we have commercialized EI in1969 using by WENKER Method, NIPPON SHOKUBAI have pursued production method, which minimized waste disposal, and successfully developed "The Vapor Phase Method", which ecologically materialize minimal resource. This was the first development in the world using by own developed new catalyst technology in 1990.

As the result of making best efforts to utilize high reactivity of EI, NIPPON SHOKUBAI would develop Ethyleneimine derivatives such as pharmaceutical intermediate products, amine containing polymers and cross-linking agents.

We would like to present standard types of El derivatives,

**EPOMIN** (Polyethyleneimine),

**POLYMENT** (Aminoethylated acrylic polymer) in this catalogue.



# **EPOMIN**

## (Polyethyleneimine)

**EPOMIN** is the water soluble polymer which is made by polymerization of ethyleneimine.

**EPOMIN** is not aentirely linear polymer but a partly branched polymer containing primary, secondary, and tertiary amine.

#### Characteristics

- ▶The highest cation density among other existing materials.
- ▶ Very high reactivity.
- ▶Water solubility.

# **Production method of €POMIN**

$$H_2C$$
 $CH_2$ 
 $H_2N$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 
 $NH_2$ 

# **Product line of EPOMIN**

	Product	SP-003	SP-006	SP-012	SP-018	SP-200	P-1050	
	Mw	300	600	1,200	1,800	10,000	70,000	
	Resin cont.(wt%)	>98	>98	>98	>98	>98	50±2	
Spec.	Viscosity (mPa·s-25°C)	200 -500	500 -2,500	3,500 -7,500	8,500 -15,000	40,000 -150,000	10,000 -20,000	
	pH (5%aq.)	10-12						
	Appearance	Colorless or light yellow liquid						

▶ Packagetype

05

Can (18kg), Drum (200kg)

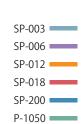
Please contact on other package types.

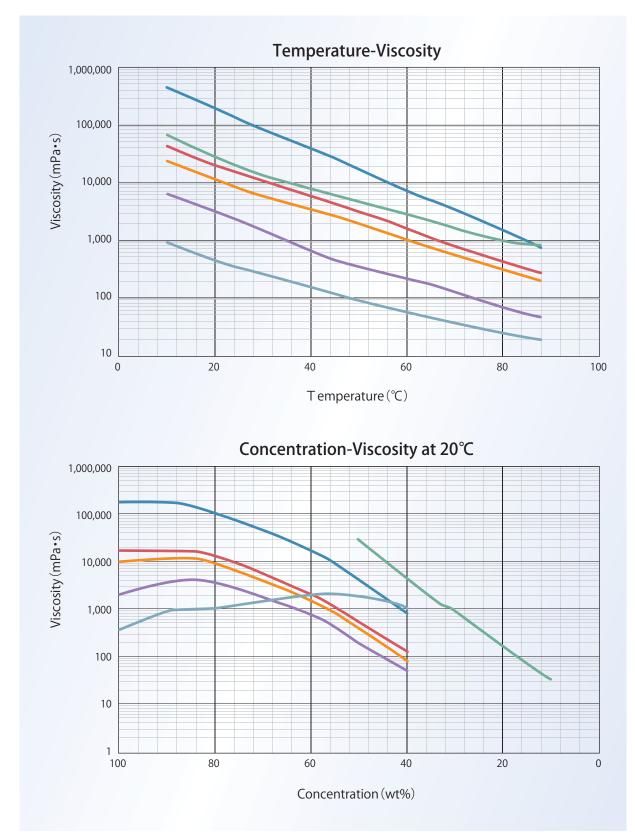
# Viscosity of **EPOMIN**

Viscosity of **EPOMIN** shows a great dependence on its molecular weight, temperature and concentration.

Polation of viscosity to temperature and concentration of **EPOMIN** 

Relation of viscosity to temperature and concentration of **EPOMIN** is shown below.





06

\* Molecular weight is not in specification.

# Chemical reactivity of **EPOMIN**

Having diversity in chemical reactivity like low molecular amine, **EPOMIN** can be modified chemically in variety. Typical examples of **EPOMIN** reactivity are illustrated below.

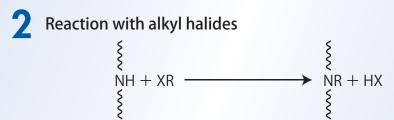
Reaction with aldehydes and ketones

$$\begin{cases} & \text{OH} \\ & \text{NH} + \text{O} = \text{C} - \text{R} \end{cases}$$

$$\begin{cases} & \text{OH} \\ & \text{I} \\ & \text{N} - \text{C} - \text{F} \end{cases}$$

$$\begin{cases} & \text{I} \\ & \text{R} \end{cases}$$

**EPOMIN** can form cross-link through reaction with dialdehyde.



**EPOMIN** can form cross-link through reaction with alkylenedihalide.

Reaction with isocyanates and thioisocyanates 
$$\begin{cases} & & & \\ &$$

**EPOMIN** reacts with alkylisocyanate.

4 Reaction with acryloyl compounds

$$\begin{cases}
NH + CH_2 = CHCOOR \longrightarrow N - CH_2CH_2COOR
\end{cases}$$

**EPOMIN** reacts with acryl monomers.

5 Reaction with epoxy compounds

$$\begin{cases}
R & R \\
NH + R_2C
\end{cases}$$

$$\begin{cases}
R & R \\
I & I \\
N - C - C - OH \\
R & R
\end{cases}$$

**EPOMIN** reacts epichlorohydrin. 6 Reaction with cyanamide, guanidine, ureaandetc.

**EPOMIN** reacts with cyanamide, quanidine and urea.

Reaction with acid, acid anhydrides and acylhalides

**EPOMIN** reacts with fatty acid.

# **Functions and Applications of €POMIN**

#### 1) Functions of **EPOMIN**

#### ▶ High adhesion and absorption

Amino group form hydrogen bond with hydroxyl group.

Amino group form ionic bond with carboxyl group.

Amino group form an organic bond with carbonyl group.

**EPOMIN** has polar group(amino group) and hydrophobic group(-CH<sub>2</sub>CH<sub>2</sub>-) in a structure and therefore has adhesion ability with different materials.

They apply these total bonding strength, and it is used adhesives, inks, paints and pressure sensitive adhesives.

#### **▶** Highcationic

**EPOMIN** is present as polycation in water and they are neutralized every anionic material. And **EPOMIN** has chelation ability of heavy metal ions.

They used paper manufacturing, water treatment conditioning, plating bath agent and dispersing agent.

#### ► High reactivity

The primary and secondary amino group easily reacts with epoxy, aldehyde, isocyanate compounds and acid gases. They used in hardening agent of epoxy resins, aldehyde adsorbents and dye fixing agents.

#### 2) Industrial applications of **EPOMIN**

Field	Applications	Recommended Products	Characteristics
Paper	Paper making agent	P-1050	Neutralization of an anion charging material Retention agent Pitch controller White water treatment Dispersion and retention of ketene dimmer
	Pressure sensitive adhesion	SP-200 P-1050	Improve in holding power
	PVC sol adhesive	SP-018 SP-200	Adhesion promoter
Adhesion	Water based adhesive	SP-200 P-1050	Adhesion promoter for EVA, Poly vinyl acetate, PVA and Acryl emulsion.
Adricsion	Anchor coat agent for extrusion laminate	P-1050	Adhesion promoter for extrusion polyethylene with Paper, Olefin film.
	Anchor coat agent for gas barrier film	P-1050	Adhesion promoter for PVA, EVOH with Olefin film
	Release agent	RP-20	Backside release agent for the various tapes.
Paint / ink	Polyvinylbutyral based ink	SP-200	Adhesion promoter.
	Acryl emulsion based paint	SP-012 SP-018	Fast drying, adhesion promoter and water resistance

Field	Applications	Recommended Products	Characteristics
	Dye fixing agent	P-1050	Washing resistance and dyeing promoters
Textile	Surface modification of tire cord	P-1050	Adhesion improvement PET cord with rubber.
, extinc	Sizing agent for glass fiber	P-1050	Lubricity
	Fixing of firere tardant	P-1050	Retention agent for fire retardant (phosphorous type)
	Liquid clarifier	P-1050	Removal of chlorine and aldehydes.
Liquid cleaning	Coagulant	P-1050	Anionic trash scavenging, charge modification and emulsion breaking
	Bacterial cell flocculant agent	P-1050	Bacteria removal
	Chelatingagent	P-1050	Metal extraction
Gas cleaning	Gas scavenger	P-1050	Absorb of C02, NOx, SOx, Cl2 and aldehydes.
Dispersion	Dispersing agent	SP-012	EPOMIN can disperse ceramic, carbon black, coal, cement, metal powder, pigment.
Metal plating	Metal plating bath agent	SP-006	Brightener, smooth agent for Zn plating.
Metal plating	Corrosion inhibitor for acid pickling, Primary rust inhibitor	P-1050	Corrosion inhibitor for iron.
Enzyme immobilization	Immobilized enzyme, Microorganism immobilized carrier	P-1050	Fixation agent to carrier for enzyme, microorganism.
Petroleum	Petroleum emulsion breaker, Fluid loss agent	P-1050	Fluid loss agent for cement slurry.
Antimicrobe /	Antibacterial / Sanitization polymer	P-1050	Ag, Cu complex PEI shows antibacterial.
preservation	Wood preservative, Cut flowers preservative	SP-018	PEI complex (Ag, Cu / PEI) shows antibacterial and permeabillity.

<sup>\*\*</sup> In using our products ( **EPOMIN** ) in relation to the application referred to in this booklet, please pay attention to existence of the intellectual property rights (including patent and its application) owned by any third parties and avoid the possible infringement of such intellectual property rights. NIPPON SHOKUBAI shall in no event be responsible for any damages or liabilities caused by infringement or alleged infringement of said intellectual property rights due to the above-mentioned use of our products.

# Propertys of **EPOMIN**

	Product	SP-003	SP-006	SP-012	SP-018	SP-200	P-1050	
	Molecular weight	300	600	1,200	1,800	10,000	70,000	
	Specific gravity	1.01	1.03	1.04	1.04	1.05	1.08	
	Amine value (mmol / g,solid)	21	20	19	19	18	18	
	Freezing point(°C)	< -20						
>	Decomposition Temperature(°C)	240	270	290	300	310	300	
Propety	Flash point(°C)	188	263	262	264	262	_	
_	Aminerate(%) Primary Secondary Tertiary	45 35 20		35 35 35 30 2				
	Solubility <sup>(*1)</sup> Water Alcohol Ethyl acetate THF Toluene n-Hexane	O O A A A X	О О Д Д Х	0 0 0 0 0 0 0	О О О О О А	O O A A X	O O X X X	
	Acute oral toxicity LD50(ml/kg. mouse)	_	1.2	1.0	0.87	2.97	8.0(*2)	
ty	Acute dermal toxicity LD50(g/kg. rat)	1.6	1.8	>2.0	>2.0	>2.0	>2.0	
Safety	Primary ski irritation(rabbit)	Moderate	Moderate	Sight	Sight	Sight	Non	
	Ames test	Positive	Negative	Negative	Negative	Negative	Negative	
TSCA (CAS No.) Listed (106899-94-9) Listed (9002-98-6)					Listed (9002-98-6 or 68130-97-2)			
	Regulatory information except U.S.A. please refer to SDS.							

\*1 ○:Soluble, △:Partly soluble, ×:Insoluble \*2As P-1000 \*3 As P-1050

#### ▶ Analysis methods

- 1.Mecular weight (1) SP series: Number average molecular weight (Mn) by ebullioscopic method.
  - (2) P series: Number average molecular weight (Mn) by osmotic pressure method.
- 2.Amine value:Acidimetry in non-qaueous system
- 3.Decomposition temperature: Differential scanning calorimetry (DSC) was used in N2 atmosphere.
- 4. Flash point : Cleveland open tester
- 5.Amine rate: NMR(13C)

# Use in the food field and Handling of **EPOMIN**

#### Use in the food field of **EPOMIN**

When I use EPOMIN in the food field, please confirm regulations / statute related to safety.

#### ► FDA information :

2)Paperboard industry

FDA publication circumstance of Polyethyleneimine

Polyethyleneimine having CAS No .9002-98-6 is published by the following 1), 2), of 3).

In addition, polyethyleneimine having CAS No .68130-97-2 is published by the

following short-term work of 4).

1)Adhesive industry : Part 175 Indirect food additives:Adhesive coating and component.

•175.105 Adhesives

•175.320 Resinous and polymeric coatings for polyolefin films.

: Part 176 Indirect food additives: Paper and paperboard components.

•176.170 Components of paper and paperboard in contact with aqueous

and fatty food. (Limited to use at a level not to exceed 5% by weight of finished day paper or paperboard fibers.)

finished dry paper or paperboard fibers.)

•176.180 Components of paper and paperboard in contact with dry food. (Limited to use at a level not to exceed 5% by weight of finished dry paper

or paperboard fibers.)

3)Food package : Part 177 Indirect food additives: Polymers

•177.1200 Cellophane

•177.1400 Water-insoluble hydroxyethyl cellulose film.

4) Enzyme industry : Part 173 Secondary direct food additives permitted in food for human consumption.

•173.357 Materials used for fixing agent in the immobilization of enzyme preparations.

#### Handling precaution of **EPOMIN**

1)Storage stability

- ▶SP series are stable for about one year when stored at a cool and dark place. However, if they contact with air (oxygen) under high temperature (>80°C) may cause their quality degradation such as coloring and surface filming.
- SP series require careful handling because of their high hygroscopicity and absorbency of carbondioxide in the air.
- ▶ P Series are stable for about one year when stored at a cool and dark place. However, if they contact with air (oxygen) under high temperature (>80'C) may cause their quality degradation such as coloring.
- P-Series require careful handling because of its absorbency of carbon dioxide in the air.

2)Heating of container

The container **EPOMIN** is inner-coated with synthetic resin.

When heated long at high temperature, the container coating may come off and the product may be colored.

If necessary, heating should be done with hot water at lower temperature than 80°C.

3)Applicable materials

► Suitable materials

Stainless steel, Synthetic resin (PVC,PE,PP), Synthetic resin coating (such as epoxy)

► Not Suitable materials

•Iron materials such as soft iron.

\*Should be avoided to prevent coloring caused by rust.

\*Such materials should not be used, particularly for **EPOMIN** aqueous solution, because iron rust tends to harden polyethyleneimine in the solution.

•Copper and copper-containing alloys such as brass

\*React with polyethyleneimine and forms bluish green complex salt

4)Storage condition

Keep away from direct sunlight, rain, heat and flame. Keep container closed and store in a dark and cool place when not in use.

Note

Please refer to the Safety Data Sheet (SDS) that provides details of the safety of the product. Above-mentioned regulations are valid September, 2013.

# **Specialty Polyethyleneimine**

The introduce specific modified polyethyleneimine.

#### 1) Octadecyl isocyanate modification polyethyleneimine

RP-20 is addition product of polyethyleneimine with octadecyl isocyanate, it has two functional group polymers having hydrophilic amino group and lipophilic ( $C_{18}$ ).

RP-20 shows superior effects as release agent of pressure-sensitive adhesive tape, and can apply polyester, polyethylene, polypropylene, cellophane and paper for base material.

	Product	RP-20	
	Appearance	Slight yellow powder	
Spec.	Melting point(℃)	87.0~95.0	
эрсс.	Toluene solubility (10℃)	Not muddiness	
	Loss on drying (wt%)	<2.0	
	Recommended diluent solvent	Toluene	
Property	Solubility	Dissolble in toluene, xylene Insoluble in water, alcohol	
	Acute oral toxicity LD50 (mg/kg.rat)	>2000	
Safety	Skin irritation (rabbit)	Not	
	Ames test	Negativity	
	Dust explosion	Lower explosive limit:40g/m <sup>3</sup>	
	TSCA (CAS No.)	Listed (68441-25-8)	

#### 2) Propylene oxide modification polyethyleneimine

PP-061 is the addition product of polyethyleneimine with propylene oxide, it is the tertiary polyamine.

	Product	PP-61	
	Appearance	Viscosity transparence liquid	
Spec.	Resin content(wt%)	48.0-52.0	
Spec.	Viscosity(mPa.s-25°C)	<200	
	pH(5%aq.)	10.0-12.0	
	OH value(mmol/g.solid)	9.9	
	Amine value(mmol/g.solid)	9.9	
	Molecular weight	Approx.1400	
Property	Mole ratio(OH/NH)	1.0	
	Specific gravity(20°C)	1.08	
	Amine rate	All tertiary amine	
	Solubility	Dissolble in water, alcohol	
	TSCA (CAS No.)	Not listed	

Please refer to the Safety Data Sheet (SDS) that provides details of the safety of the product. Above-mentioned regulations are valid September, 2013.

# POLYMENT

#### (Aminoethylated Acrylic Polymers)

**POLYMENT** is the primary amino group component acrylic polymer which has polyethyleneimine in side chain.

**POLYMENT** is poly acryl amine having both characteristics of poly ethyleneimine and acrylic polymer and is superior in high reactivity and adhesion of the primary amino group origin.

Generally, for cationic acrylic polymer, Dimethylaminoethyl acrylate polymer (DAA), Dimethylaminoethyl methacrylate polymer (DAM) are known, However, they are the tertiary amine or quarternary amine type. For polymer having primary amine, **POLYMENT** is only one product in the world.

#### Production method of POLYMENT

**POLYMENT** is synthesized by reaction with ethyleneimine and carboxylic acid group.

## Characteristic of POLYMENT

**POLYMENT** has water reducibility type (NK-100PM, NK-200PM), solvent type (NK-350, NK-380) The adhesives, primers, paints which blended epoxy resin with **POLYMENT** show superior adhesion to plastics and metals.

Туре	Water reducibility	Solvent	
Product	NK-100PM, NK-200PM	NK-350, NK-380	
Structure	NH2 •HX NH2 •HX HX:HCl 、HBr	NH2 NH2	
Characteristic	<ul> <li>Water soluble polymer</li> <li>Self emulsification type hardening agent of epoxy resin</li> <li>Room temperature reactivity with epoxy resin</li> <li>Superior adhesion</li> <li>Superior water resistance and chemical resistance</li> </ul>	•Solvent soluble polymer •Room temperature reactivity with epoxy resin •Superior adhesion •Superior water resistance, chemical resistance and barrier	
•Water based for floor paints •Primer for olefin films <b>Application</b>		<ul> <li>Primer for pressure-sensitive adhesive tape</li> <li>Adhesive promoting agents and primer for films</li> <li>Adhesives of fluorine film with Steel (NK-350)</li> <li>Antimigration agent for PVC film (NK-380)</li> </ul>	

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# Specification and property of POLYMENT

		NK-100PM (Water reducibility)	NK-200PM (Water reducibility)	NK-350 (Solvent)	NK-380 (Solvent)
	Solid cont.(wt%)	48.0-50.0	55.0-57.0	33.0-37.0	29.0-31.0
	Viscosity (mPa•s/25°C)	4000-8000	20000-40000	400-1500	<2000
	рН	4.0-5.5	4.0-5.5	-	_
Spec.	Appearance	Viscous, yellowish-brown liquid	Viscous, yellowish-brown liquid	Viscous, clear liquid	Viscous, light yellow liquid
	Water solubility	Complate	Complate	-	_
	Amino hydrogen equivalent weight (g-solid/eq.)*1	350-450	350-450	1000-1800	800-1400
	Amine value (mmol/g-solid)*2	2.2-2.9	2.2-2.9	0.6-1.0	0.7-1.3
	Tg(℃)	13	16	40	100
	MW	10,000~30,000	10,000~30,000	100,000	100,000
-ga	Spec. grav.(25°C)	1.05	1.10	0.95	0.94
Physical	Product solvent	PM	PM	Toluene/IPA (7/3)	Toluene / MIBK (3/1)
	Solubility	Dissolble in water, lower alcohol	Dissolble in water, lower alcohol	Dissolble in toluene, IPA Insoluble in water,	Dissolble in toluene, MIBK, MEK, IPA Insoluble in water
	Flash point(°C)	36(Closed Cup)	36(Closed Cup)	4(Closed Cup)	4(Closed Cup)
	Acute oral toxicity LD50(mg/kg. rat)	>5000	>5000	>5000	>5000
	Acute dermal toxicity LD50(mg/kg. rat)	>2000	>2000	>2000	>5000
ety	Primary skin irritation (rabbit)	Slight	Slight	Severe	Moderate
Safety	Acute eye irritation (rabbit)	Moderate∼ Severe	Moderate∼ Severe	Moderate∼ Severe	_
	Mutagenicity (AMES)	Positive	Positive	Positive	_
	Micronucleus test (in vivo)	Negative	Negative	Negative	Negative

	NK-100PM	NK-200PM	NK-350	NK-380
	(Water reducibility)	(Water reducibility)	(Solvent)	(Solvent)
CAS No.	67970-17-6 or 449196-55-8	103051-70-3	120363-55-5	178954-62-6

PM:Propylene glycol monomethyl ether, IPA:Isopropyl alcohol , MIBK:Methyl isobutyl ketone, MEK:Methyl ethyl ketone

- \*1 Amino hydrogen equivalent weight:Solid weight equivalent to one amine mol.
- \*2 Amine value:Amine mol number (mmol) contained in solid1g

Please refer to the Safety Data Sheet(SDS) that provides details of the safety of the product. Above-mentioned regulations are valid September,2012.