

— Ethyleneimine Polymer for cross bridge of creation —

EPOMIN™ POLYMENT™



NIPPON SHOKUBAI CO.,LTD.

Osaka Office
KoginBldg.
4-1-1 Koraihashi, Chuo-ku
Osaka 541-0043, Japan

Tokyo Office
Hibiya Dai Bldg
1-2-2 Uchisaiwai-cho, Chiyoda-ku
Tokyo 100-0011, Japan
URL <https://www.shokubai.co.jp/>

EPOMIN

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POLYMENT

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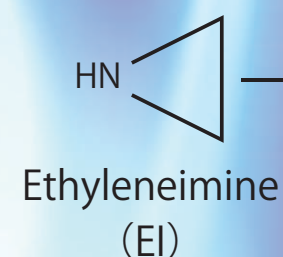
Introduction

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

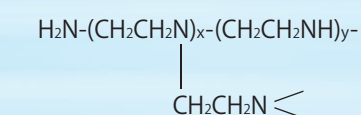
Since we have commercialized EI in 1969 using by WENKER Method, NIPPON SHOKUBAI have pursued production method, which minimized waste disposal, and successfully developed "The Vapor Phase Method", which ecologically materialize minimal resource. This was the first development in the world using by own 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 EI derivatives,
EPOMIN (Polyethyleneimine),
POLYMENT (Aminoethylated acrylic polymer)
 in this catalogue.



Polymerization



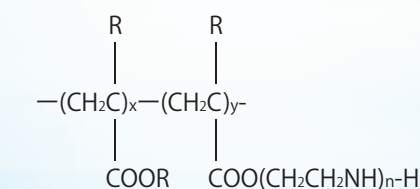
EPOMIN (Polyethyleneimine)

Modified Polyethyleneimine

PP-061 (Polyethyleneimine-Propylene oxide)

RP-20 (Polyethyleneimine-Octadecyl isocyanate)

Aminoethylation



POLYMENT (Aminoethylated Acrylic Polymers)



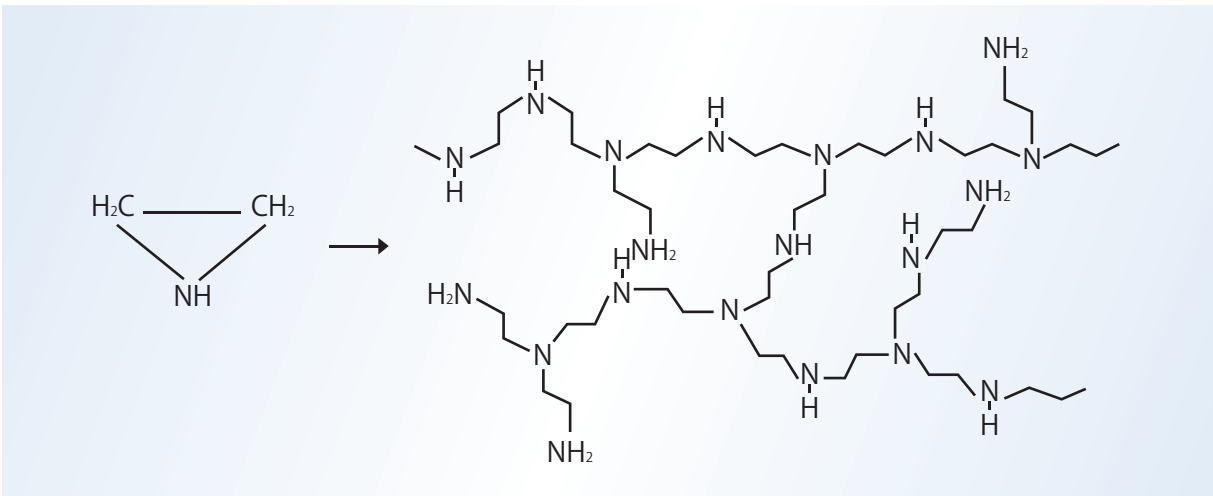
EPOMIN

(Polyethyleneimine)

Polyethyleneimine **EPOMIN** is a water-soluble polymer made by the polymerization of ethyleneimine. **EPOMIN** is not an entirely linear polymer; it has a highly-branched structure that contains primary, secondary, and tertiary amines.

- Characteristics
- ▶ It is the highest cation-dense polymer in existence.
 - ▶ It is a very high reactive polymer.
 - ▶ It is a water-soluble polymer.

Manufacturing method of EPOMIN



Product line of EPOMIN

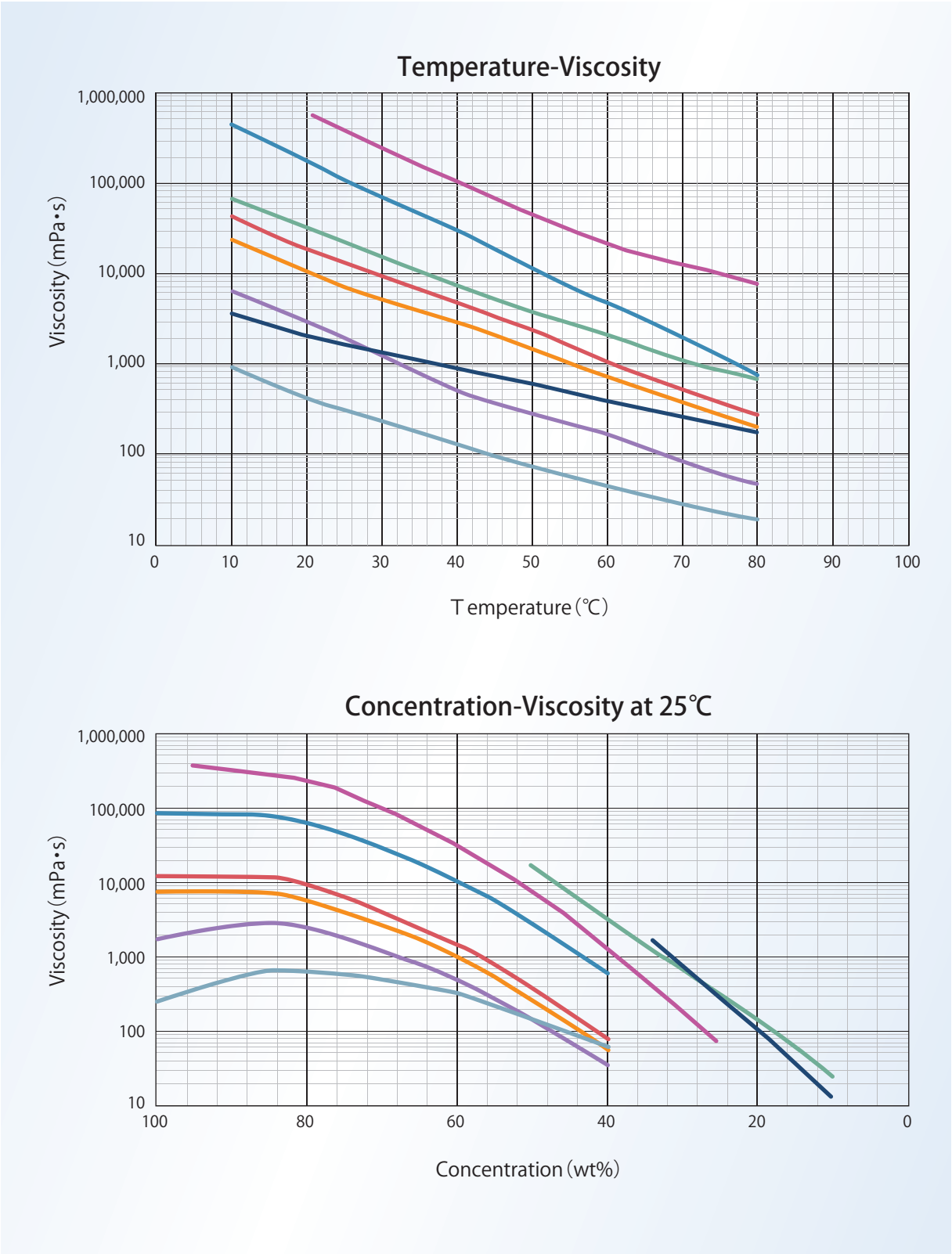
Product		SP-003	SP-006	SP-012	SP-018	SP-200	HM-2000	P-1050	P-3000 (in development)
Mw		300	600	1,200	1,800	10,000	30,000	70,000	100,000
Spec.	Resin cont. (wt%)	>98	>98	>98	>98	>98	93~95	50±2	35±1
	Viscosity (mPa·s/25°C)	200 -500	500 -2,500	3,500 -7,500	8,500 -15,000	40,000 -150,000	5,000 -15,000 (50% aqueous solution)	5,000 -15,000	1,300 -2,600
	pH (5%aq.)	10-12							
	Appearance	Colorless or light yellow liquid							

* The specs for P-3000 are provisional.
 * Molecular weight is not in specification.

Viscosity of EPOMIN

The viscosity of **EPOMIN** greatly varies depending on its molecular weight, temperature and concentration when diluted in water. The graphs below show the relationship between temperature v.s. viscosity and concentration v.s. viscosity.

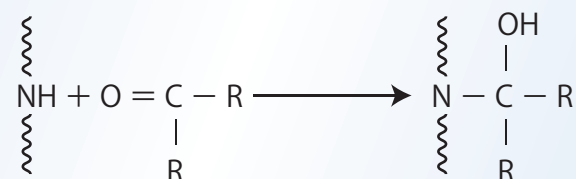
SP-003 SP-200
 SP-006 HM-2000
 SP-012 P-1050
 SP-018 P-3000



Chemical reactivity of EPOMIN

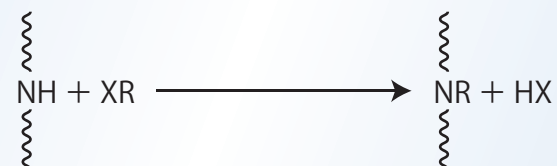
Having diversity in chemical reactivity like low molecular amine, **EPOMIN** can be modified chemically in variety. Typical examples of **EPOMIN** reactivity are illustrated below.

1 Reaction with aldehydes and ketones



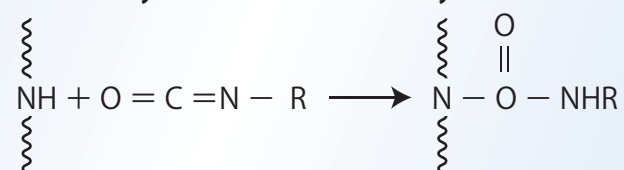
EPOMIN can form cross-link through reaction with dialdehyde.

2 Reaction with alkyl halides



EPOMIN can be alkylated with alkyl halides.

3 Reaction with isocyanates and thioisocyanates



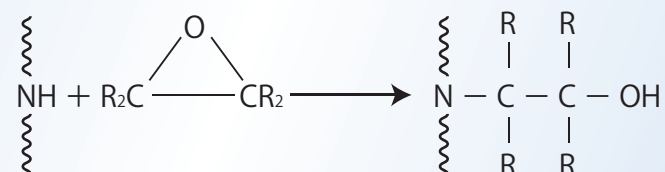
EPOMIN reacts with isocyanates.

4 Reaction with acryloyl compounds



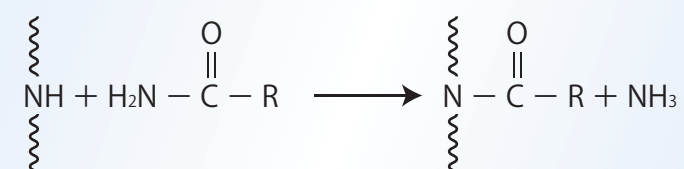
EPOMIN reacts with acrylic monomers. (Michael addition)

5 Reaction with epoxy compounds



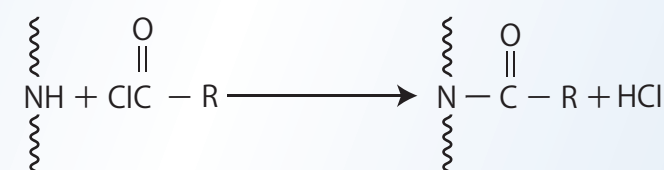
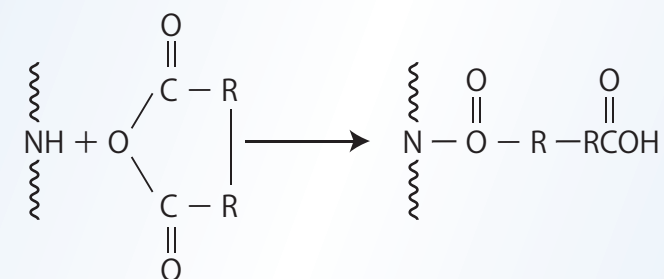
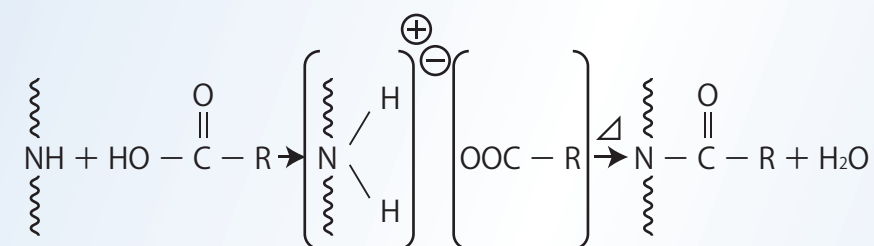
EPOMIN reacts with epoxy compounds.

6 Reaction with cyanamide, guanidine, urea.



EPOMIN reacts with cyanamide, guanidine and urea.

7 Reaction with acid, acid anhydrides and acylhalides



EPOMIN reacts with carboxylic acid derivatives.

Functions and Applications of EPOMIN

1) Functions of EPOMIN

►High adhesion and absorption

The amino group forms hydrogen bonds with hydroxyl group, ionic bonds with carboxyl group, and covalent bonds with the aldehyde group and ketone group. **EPOMIN** also has polar group (amino group) and hydrophobic group (ethylene group) in its structure, which enhances its bonding force with materials of different polarities. These comprehensive bonding forces of **EPOMIN** are utilized in fields such as adhesion, ink, paint, and pressure-sensitive adhesive agents.

►High cationicity

EPOMIN exists as polycation in water, and it neutralizes and adsorbs all types of anionic materials. **EPOMIN** also chelates heavy metal ions. This highly cationic property of **EPOMIN** is utilized in fields such as paper manufacturing, water treatment, plating bath agents, dispersants, etc.

►High reactivity

Because of its reactive primary and secondary amino group, **EPOMIN** easily reacts with epoxy, aldehyde, isocyanate compounds, and acid gases. This highly reactive property of **EPOMIN** is utilized in the modification 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
Adhesion	Pressure sensitive adhesion	SP-200 P-1050	Improve in holding power
	PVC sol adhesive	SP-018 SP-200	Adhesion promoter
	Water based adhesive	SP-200 P-1050	Adhesion promoter for EVA, Poly vinyl acetate, PVA and Acryl emulsion.
	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
Textile	Dye fixing agent	P-1050	Washing resistance and dyeing promoters
	Surface modification of tire cord	P-1050	Adhesion improvement PET cord with rubber.
	Sizing agent for glass fiber	P-1050	Lubricity
	Fixing of fire retardant	P-1050	Retention agent for fire retardant (phosphorous type)
Liquid cleaning	Liquid clarifier	P-1050	Removal of chlorine and aldehydes.
	Coagulant	P-1050	Anionic trash scavenging, charge modification and emulsion breaking
	Bacterial cell flocculant agent	P-1050	Bacteria removal
	Chelating agent	P-1050	Metal extraction
Gas cleaning	Gas scavenger	P-1050	Absorb of CO ₂ , NO _x , SO _x , Cl ₂ 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.
	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 / preservation	Antibacterial / Sanitization polymer	P-1050	Ag, Cu complex PEI shows antibacterial.
	Wood preservative, Cut flowers preservative	SP-018	PEI complex (Ag, Cu / PEI) shows antibacterial and permeability.

※ 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.

Properties of EPOMIN

Product		SP-003	SP-006	SP-012	SP-018	SP-200	HM-2000	P-1050	P-3000 (in development)
Property	Molecular weight	300	600	1,200	1,800	10,000	30,000	70,000	100,000
	Specific gravity	1.01	1.03	1.04	1.04	1.05	1.04	1.08	1.05
	Amine value (mmol / g-solid)	21	20	19	19	18	18	18	18
	Freezing point(°C)	< -20						< -15	< -10
	Decomposition Temperature(°C)	240	270	290	300	310	314	300	300
	Flash point(°C)	188	263	262	264	262	262	—	—
	Amine ratio(%) Primary Secondary Tertiary	45 35 20	35 35 30				34 35 31	25 50 25	30 40 30
	Solubility ^(※1) Water Alcohol Ethyl acetate THF Toluene n-Hexane	○ ○ △ △ △ ×	○ ○ △ △ △ ×	○ ○ △ △ △ ×	○ ○ △ △ △ ×	○ ○ △ △ × ×	○ ○ × × × ×	○ ○ × × × ×	○ ○ × × × ×
	Acute oral toxicity LD ₅₀ (mg/kg. mouse)	—	1.2	1.0	0.87	2.97	2.97	8.0 ^(※2)	8.0
	Acute dermal toxicity LD ₅₀ (g/kg. rat)	1.6	1.8	>2.0	>2.0	>2.0	>2.0	>2.0	>2.0
Safety	Skin irritation (rabbit)	Moderate	Moderate	Slight	Slight	Slight	Slight	None	None
	Ames test	Positive	Negative	Negative	Negative	Negative	Negative	Negative	Negative
CAS No.		106899-94-9				9002-98-6		9002-98-6 or 68130-97-2	9002-98-6

※1 ○ : Soluble, △ : Partly soluble, × : Insoluble

The above properties are representative values and are not guaranteed.

► Analysis methods

1. Molecular 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-aqueous system
3. Decomposition temperature : Differential scanning calorimetry (DSC) was used in N₂ atmosphere.
4. Flash point : Cleveland open tester
5. Amine ratio : 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 :

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.
- 2) Paperboard industry : 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 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, HM-2000)
► This product will keep stable for about one year when stored in a cool and dark place. However, if the product comes into contact with the air (oxygen), its quality may deteriorate such as coloring occurring or film forming on the surface.
► Please take care when storing the product, as it is highly hygroscopic, and absorbs carbon dioxide gas in the air.
(P-1050, P-3000)
► This product will keep stable for about one year when stored in a cool and dark place. However, if the product comes into contact with the air (oxygen), its quality may deteriorate such as coloring occurring.
► Please take care when storing the product, as it absorbs carbon dioxide gas 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.

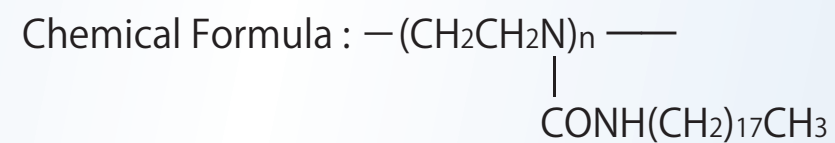
Modified Polyethyleneimine

1) Octadecyl isocyanate modified polyethyleneimine

RP-20 is the modified polyethyleneimine reacted with octadecyl isocyanate.

RP-20 has two functionalities: being in the hydrophilic amino group and lipophilic (hydrophobic: C18).

By using these functions, RP-20 shows an exceptional effect as a rear-side release agent of pressure-sensitive adhesive tape which base materials are polyester, polyethylene, polypropylene, cellophane, and paper, etc.

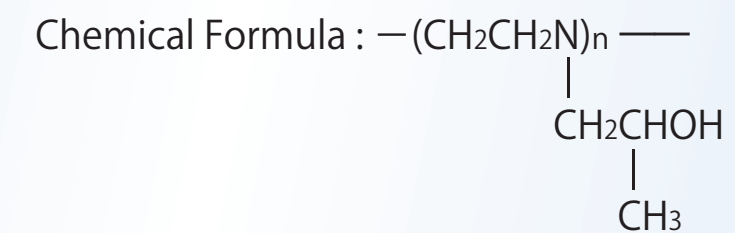


Product		RP-20
Spec.	Appearance	Slight yellow powder
	Melting point(°C)	87.0~95.0
	Toluene solubility (10°C)	No turbidity
	Loss on drying (wt%)	<2.0
Property	Recommended diluent solvent	Toluene
	Solubility	Soluble in toluene, xylene Insoluble in water, alcohol
Safety	Acute oral toxicity LD50 (mg/kg.rat)	>2000
	Skin irritation (rabbit)	None
	Ames test	Negative
	Dust explosion	Lower explosive limit:40g/m³
CAS No.		68441-25-8

2) Propylene oxide modified polyethyleneimine

PP-061 is the addition product of polyethyleneimine with propylene oxide,

it is the tertiary polyamine.



Product		PP-061
Spec.	Appearance	transparence liquid
	Resin content(wt%)	48.0-52.0
	Viscosity(mPa•s/25℃)	<200
	pH(5%aq.)	10.0-12.0
Property	OH value(mmol/g-solid)	9.9
	Amine value(mmol/g-solid)	9.9
	Molecular weight	Approx.1400
	Mole ratio(OH/N)	1.0
	Specific gravity(20℃)	1.08
	Amine ratio	All tertiary amine
	Solubility	Soluble in water, alcohol
	CAS No.	Not registered

POLYMENT

(Aminoethylated Acrylic Polymers)

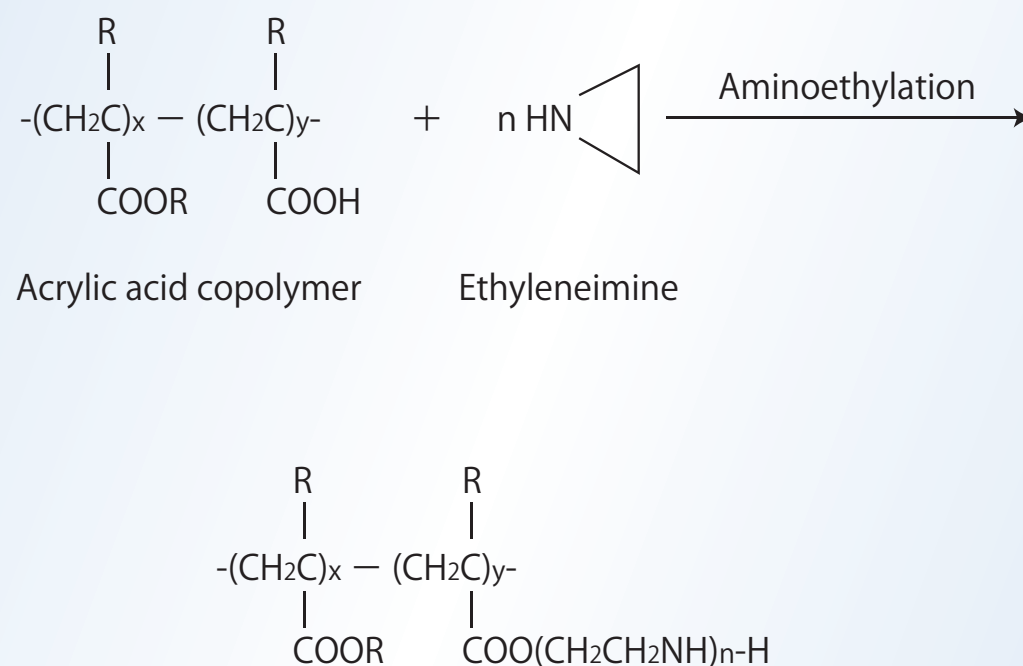
POLYMENT is an acrylic polymer containing primary amino group due to the grafting of polyethyleneimine in its side chain.

POLYMENT is a polyacrylamine that has the features of both polyethyleneimine and acrylic polymer. **POLYMENT** shows high reactivities thanks to its amino group and superior adhesiveness to various base materials. Cationic acrylic polymers are generally known as being tertiary amine and quaternary ammonium polymers, such as dimethylaminoethyl acrylate or dimethylaminoethyl methacrylate polymer.

POLYMENT is the only cationic acrylic polymer with primary amine in the world.

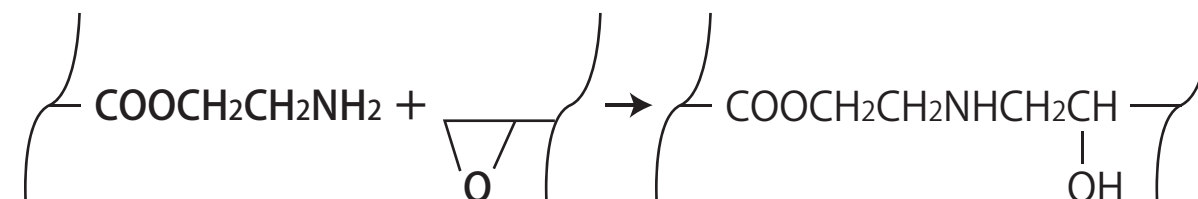
Manufacturing method of POLYMENT

Using the reactivity of ethyleneimine and carboxyl groups, acrylic acid copolymers can be easily converted to acrylic polymers with primary amines.



Characteristic of POLYMENT

POLYMENT is grouped into two types according to its form. Type one is a water-dilutable resin that can be diluted in water by neutralizing amino groups, and type two is a solvent-based resin that is synthesized under solvent conditions. Both types have primary amino groups, which gives them excellent reactivity with epoxy resins, and superior adhesion to base materials such as plastics and metals, etc.



Type	Water dilutable	Solvent based
Product	NK-100PM, NK-200PM	NK-350, NK-380
Structure	$ \begin{array}{c} \text{---} \\ \quad \\ \text{NH}_2 \cdot \text{HX} \quad \text{NH}_2 \cdot \text{HX} \\ \text{HX: HCl, HBr} \end{array} $	$ \begin{array}{c} \text{---} \\ \quad \\ \text{NH}_2 \quad \text{NH}_2 \end{array} $
Characteristic	•Water soluble •Self emulsification type hardening agent of epoxy resin •Room temperature reactivity with epoxy resin •Superior adhesion •Superior chemical resistance	•Solvent soluble •Room temperature reactivity with epoxy resin •Superior adhesion •Superior water and chemical resistance, and barrier property
Application	•Water based for floor paints •Primer for olefin films	•Primer for pressure-sensitive adhesive tape •Adhesive promoting agents and primer for films •Adhesives of fluorine film with Steel (NK-350) •Antimigration agent for PVC film (NK-380)

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Specifications and properties of POLYMENT

		NK-100PM (Water dilutable)	NK-200PM (Water dilutable)	NK-350 (Solvent based)	NK-380 (Solvent based)
Spec.	Solid cont.(wt%)	48.0-50.0	55.0-57.0	33.0-37.0	29.0-31.0
	Viscosity (mPa•s/25℃)	4000-8000	20000-40000	400-1500	<2000
	pH	4.0-5.5	4.0-5.5	—	—
	Appearance	Viscous, yellowish-brown liquid	Viscous, yellowish-brown liquid	Viscous, clear liquid	Viscous, light yellow liquid
	Water solubility	Complete	Complete	—	—
	Amino hydrogen equivalent weight (g-solid/eq.)*1	350-450	370-470	1000-1800	800-1400
Physical	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
	Spec. grav.(25℃)	1.05	1.10	0.95	0.94
	Product solvent	PM	PM	Toluene/IPA (7/3)	Toluene / MIBK (3/1)
	Solubility	Soluble in water, lower alcohol	Soluble in water, lower alcohol	Soluble in toluene, IPA Insoluble in water,	Soluble in toluene, MIBK, MEK, IPA Insoluble in water
	Flash point(℃)	36(Closed Cup)	36(Closed Cup)	4(Closed Cup)	4(Closed Cup)
Safety	Acute oral toxicity LD50(mg/kg. rat)	>5000	>5000	>5000	>5000
	Acute dermal toxicity LD50(mg/kg. rat)	>2000	>2000	>2000	>5000
	Skin irritation (rabbit)	Slight	Slight	Severe	Moderate
	Acute eye irritation (rabbit)	Moderate~ Severe	Moderate~ Severe	Moderate~ Severe	—
	Mutagenicity (AMES)	Positive	Positive	Positive	—
	Micronucleus test (in vivo)	Negative	Negative	Negative	Negative

PM : Propylene glycol monomethyl ether

IPA : Isopropanol (Isopropyl alcohol)

MIBK : Methyl isobutyl ketone

MEK : Methyl ethyl ketone

* 1 Amino hydrogen equivalent weight : Solid weight (g) equivalent to 1 amine mol.

* 2 Amine value : mmol number of amine contained in 1 g of solid