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Introduction

Epocros has been introduced to the market by Nippon Shokubai as world’s first commercialization of Oxazoline related product built on the basic technique of Dow Chemical Company USA as well as the accumulated knowledge of Nippon Shokubai on synthetic organic chemistry and polymer science.

Recently, worldwide expectation for developing environmentally safe product is becoming prevalent and the trend is being accelerated toward the waterborne product against VOC and solvent. With those background, Epocros is accepted and utilized by variety of customers. Especially, as Epocros is realized on polymer structure which is quite rare for the crosslinkers, the market is recognizing it as a crosslinker with extremely high safety.

This document provides the characteristics of each Epocros series with supplementary technical data which can be used for examples. If you need detailed technical information, contact our sales division.

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General Information of EPOCRS

Classification of EPOCRS

Product line-up, properties and characteristics

<table>
<thead>
<tr>
<th>Product Type</th>
<th>Emulsion</th>
<th>Water soluble</th>
</tr>
</thead>
<tbody>
<tr>
<td>Series name</td>
<td>K-2000 Series</td>
<td>WS Series</td>
</tr>
<tr>
<td></td>
<td>WS-300</td>
<td>WS-500</td>
</tr>
<tr>
<td>Appearance</td>
<td>Milky white emulsion</td>
<td>None~Clear Red Liquid</td>
</tr>
<tr>
<td>Type</td>
<td>Soft</td>
<td>Middle</td>
</tr>
<tr>
<td></td>
<td>High oxazoline VOC free</td>
<td>Standard</td>
</tr>
<tr>
<td>Nonvolatiles(%)</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>Solvent</td>
<td>Water</td>
<td>Water</td>
</tr>
<tr>
<td>pH</td>
<td>7-9</td>
<td>7-10</td>
</tr>
<tr>
<td>Main components</td>
<td>Styrene/Acrylic</td>
<td>Acrylic</td>
</tr>
<tr>
<td>WPO*¹</td>
<td>550</td>
<td>130</td>
</tr>
<tr>
<td>Tg(°C)</td>
<td>-50*¹</td>
<td>0°³</td>
</tr>
<tr>
<td>Molecular Weight*²</td>
<td>Mn N/A°⁶</td>
<td>4×10⁴</td>
</tr>
<tr>
<td></td>
<td>Mw N/A°⁶</td>
<td>12×10⁴</td>
</tr>
</tbody>
</table>

Common characteristics

- VOC free, Long Pot life for one packaging
- Controllable appearance by Tg adjustment
- Improve water resistance, heat resistance and film properties
- Adhesion promoting particularly to polyester
- Fast drying
- Low-toxicity
- Long Pot life one packaging
- Higher reactivity in comparison with emulsion type
- Improve water resistance, heat resistance and film properties
- Adhesion promoting for PET, OPP, PVC etc.
- Fast drying
- Low-toxicity

Figures shown in the above table are representative values; these are not to be considered product specification.

*¹ Equivalent Weight (Weight per oxazoline equivalent: nonvolatile g/eq); Theoretical value
*² Oxazoline value (mmol/g, nonvolatile); Theoretical value
*³ Calculated value
*⁴ Actual measurement
*⁵ Molecular weight (HPLC, g/mol)
*⁶ N/A: not available
*⁷ 1-Methoxy-2-propanol
Reactivity of the Oxazoline groups

### Reaction with the carboxyl groups

1. Reaction with carboxyl groups which is contained in most of waterborne polymers is regarded to have the highest reactivity.
2. After the reaction with the carboxyl groups, stable amid ester bonding is formed. Any by-product will not be generated.
3. Reaction with carboxyl groups proceeds rapidly at elevated temperature 80°C to 100°C.
4. Reaction with carboxyl groups proceeds slowly at room temperature.
5. Oxazoline groups have better reactivity with carboxyl groups than with epoxy groups.
6. Oxazoline groups also react with aromatics such as thiol groups as well as phenol groups, but oxazoline groups cannot react with alcoholic hydroxyl groups.

![Schematic reaction between Carboxyl groups and Oxazoline groups](image)

Crosslinked structure (Amide ester bonding)

Model reaction of Oxazoline groups (Ethyl Oxazoline / Propionic acid)

![Model reaction of Oxazoline / Carboxyl groups](image)

![Comparison between the reactivity of Oxazoline groups and Epoxy groups](image)

### Safety and worldwide Regulatory

#### EPOCROS is a low toxic and highly safe crosslinker

- **Safety data**

<table>
<thead>
<tr>
<th></th>
<th>Ames test</th>
<th>Skin temporary irritant test (Rabbit)</th>
<th>Acute toxicity (Oral, Rat, LD50)</th>
<th>Fish toxicity (Killfish, LC50, 96hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-2010E</td>
<td>Negative</td>
<td>None</td>
<td>&gt;2000mg/kg</td>
<td>&gt;1000mg/L</td>
</tr>
<tr>
<td>K-2020E</td>
<td>Negative</td>
<td>None</td>
<td>&gt;2000mg/kg</td>
<td>&gt;1000mg/L</td>
</tr>
<tr>
<td>K-2030E</td>
<td>Negative</td>
<td>None</td>
<td>&gt;2000mg/kg</td>
<td>&gt;1000mg/L</td>
</tr>
<tr>
<td>WS-300</td>
<td>Negative</td>
<td>Slight irritation PlI=0.2</td>
<td>&gt;2000mg/kg</td>
<td>N/A</td>
</tr>
<tr>
<td>WS-500</td>
<td>Negative</td>
<td>None</td>
<td>&gt;2000mg/kg</td>
<td>&gt;1000mg/L</td>
</tr>
<tr>
<td>WS-700</td>
<td>Negative</td>
<td>None</td>
<td>&gt;2000mg/kg</td>
<td>&gt;1000mg/L</td>
</tr>
</tbody>
</table>

N/A : not available

- **World wide Regulatory**

<table>
<thead>
<tr>
<th>Law / Inventory Country / regions</th>
<th>Law concerning the Examination and Regulation of Manufacture,etc.of Chemical substances</th>
<th>TSCA USA</th>
<th>REACH EU (EEA)</th>
<th>AREC (K-REACH) Korea</th>
<th>IECSC China</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-2010E</td>
<td></td>
<td>○</td>
<td>○*</td>
<td>○**</td>
<td>X</td>
</tr>
<tr>
<td>K-2020E</td>
<td></td>
<td>○</td>
<td>○*</td>
<td>○**</td>
<td>X</td>
</tr>
<tr>
<td>K-2030E</td>
<td></td>
<td>○</td>
<td>○*</td>
<td>○**</td>
<td>X</td>
</tr>
<tr>
<td>WS-300</td>
<td></td>
<td>○</td>
<td>×</td>
<td>×</td>
<td>X</td>
</tr>
<tr>
<td>WS-500</td>
<td></td>
<td>○</td>
<td>○*</td>
<td>○**</td>
<td>X</td>
</tr>
<tr>
<td>WS-700</td>
<td></td>
<td>○</td>
<td>○*</td>
<td>○**</td>
<td>X</td>
</tr>
</tbody>
</table>

○ : Registered
○* : Registered under limited tonnage
○** : Phase in substance
X : Not Registered

Conditions on Reactivity: Ethyl oxazoline / Propionic acid = 1/1 (mol/mol), solvent-free reaction
Method of analysis: Gas chromatography analysis
General formulating consideration:

If we could suppose that the reaction proceeds just like the theory, optimum quantity of Epocros as an additive is 100mol%. However, under the effects of reacting conditions as well as the effects of other additives, 20 to 100mol% is considered to be recommended in actual usages.

### Amount of the Oxazoline group contained in the EPOCROS (per g.NV*)

<table>
<thead>
<tr>
<th></th>
<th>K-2000 Series</th>
<th>WS-300</th>
<th>WS-500</th>
<th>WS-700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of the Oxazoline group (mmol/g.NV*)</td>
<td>1.8</td>
<td>7.7</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Nonvolatiles(wt%)</td>
<td>40.0</td>
<td>10.0</td>
<td>39.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Caution: Each value is theoretically calculated, not to be considered as specification.

### Calculating method of the amount of Epocros additive regarding the amount of the base resin (Calculation of mol to be added)

Before the calculation, prepare the acid value and g.NV of the base resin as well as the amount of the Oxazoline and g.NV in the crosslinking agent.

First, get the COOH mol amount from the acid value of the base resin by using formula A. Then substitute the variables in formula B.

Formula A: COOH mol amount (mmol/g.NV*) = Acid value / 56.1 (Molecular weight of KOH: g/mol)

Acid value: Amount (mg) of the KOH potassium hydroxide which is required to neutralize the COOH groups contained in 1g of NV base resin.

COOH mol amount: Number of COOH mols contained in 1 g of NV base resin.

Formula B (Calculating method of the adding amount of Epocros):

Amount of the adding Epocros (g) = (Weight of the base resin (g) x (NV ratio of the base resin (%) / 100) x (Amount of COOH mol (mmol/g) / Amount of Oxazoline group in the Epocros (mmol/g)) / NV ratio of the Epocros (%) / 100)

For example, suppose the main acid value of the base resin is to be 30(mg KOH/g NV*) and the NV* ratio is to be 40.0%; By using the formula A, COOH mol amount of the base resin is decided to be 0.54(mmol/g NV*). (Calculation: 30/56.1 = 0.53(mmol/g NV*))

Amount to be added for K-2000 series (g) = (100 x (40 / 100) x 0.54) / 1.8 / (40 / 100) = 29.4

Amount to be added for WS-300(g) = (100 x (40 / 100) x 0.54) / 7.7 / (10 / 100) = 27.5

Amount to be added for WS-500(g) = (100 x (40 / 100) x 0.54) / 4.5 / (40 / 100) = 12.1

Amount to be added for WS-700(g) = (100 x (40 / 100) x 0.54) / 4.5 / (25 / 100) = 18.8

Example: Maximum and minimum values of recommended amounts (wt%) of Epocros to be added when each of them is used for the base resin with acid value30.

<table>
<thead>
<tr>
<th></th>
<th>K-2000 Series</th>
<th>WS-300</th>
<th>WS-500</th>
<th>WS-700</th>
</tr>
</thead>
<tbody>
<tr>
<td>20mol%</td>
<td>5.9wt%</td>
<td>5.5wt%</td>
<td>2.4wt%</td>
<td>3.8wt%</td>
</tr>
<tr>
<td>100mol%</td>
<td>29.4wt%</td>
<td>27.5wt%</td>
<td>12.1wt%</td>
<td>18.8wt%</td>
</tr>
</tbody>
</table>

* NV: Nonvolatiles

### Effect of the neutralization agent on reactivity

As Oxazoline group has quite low reactivity with Carboxylate, it has good pot life when mixed with waterborne resin which has neutralized carboxyl groups. While it is drying, as the neutralizing agents (such as ammonia or amine etc.) are being evaporated, the reaction occurs. Crosslinking speed is tend to be affected by the neutralizing agents for Carboxyl group. Therefore, when you need to harden it at low temperature, combination with the waterborne resins which have highly evaporative ammonia as its neutralizer is recommended.

### Effect of pH

- Crosslinking density is inversely related to swelling ratio. As ammoniacal neutralizers have high evaporation rate, it is rarely affected by pH at elevated temperature (80°C and 120°C).
- At room temperature (23°C), as ammoniacal neutralizer can not evaporate well, it is highly affected by pH.

### Effect of depending on types of neutralizer

- Reactivity of Epocros is affected by evaporation of neutralizer.
- At elevated temperature (120°C), neutralization by ammonia and triethylamine has similar reactivity.

---

**References**
Reactivity

- Measuring swelling ratio with Xylene ① (Observing the heating condition to be hardened)
  - By adding Epocros, swelling ratio with Xylene is suppressed, therefore solvent resistance is increased.
  - Hardening performance is significantly increased at 80° C and above.
  - WS-500 demonstrated better hardening performance than K-2020E when same amount of additives were provided.

- Measuring swelling ratio with Xylene ② (Crosslinking at room temperature)
  - By adding Epocros, swelling ratio with Xylene decreased, therefore hardening resistance increased.
  - It can be hardened under the room temperature. However, significantly long curing time is required to get enough performance.
  - WS-500 demonstrated better hardening performance than K-2020E when same amount of additives were provided.

- Film tensile strength test
  - By adding Epocros, film tensile strength of the base resin is increased.
  - Suitable Stress-Strain performance for each application can be obtained by selecting polymer Tg of K-series.

Reaction mechanism of storage stability

- The mixture of carboxylated resin and Epocros shows excellent storage stability under ambient conditions. This is attributed to blocking effect of neutralizers.
- As the neutralizer volatilizes, for example during the drying, the reaction is accelerated.
- The product can be prepared as one packaging

Stability data of one packaging condition ①

Base resin : Acrylic copolymer (Emulsion type, Acid value: 31mgKOH/g, nonvolatiles)

Storing condition: 50°C × One month after mixing

- There is no significant difference on pH, viscosity, and MFT performance when stored for one month after mixing at 50°C. The tensile strength of films formed from these mixtures show almost same value in this test.

<table>
<thead>
<tr>
<th>Added ratio(phr)*</th>
<th>WS-500</th>
<th>K-2020E</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>Functional ratio of [COOH]/[OX]</td>
<td>100/40</td>
<td>100/16</td>
<td>0</td>
</tr>
<tr>
<td>Storage period</td>
<td>Initial 1month Initial 1month Initial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>7.6</td>
<td>7.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Viscosity(mPa.s)</td>
<td>39</td>
<td>40</td>
<td>32</td>
</tr>
<tr>
<td>MFT(°C)</td>
<td>10</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>Crosslinking Characteristics</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Swelling ratio(Xylene : wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Water : wt%)</td>
<td>180</td>
<td>115</td>
<td>880</td>
</tr>
<tr>
<td>Tensile strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry(MPa)</td>
<td>12.7</td>
<td>13.2</td>
<td>7.8</td>
</tr>
<tr>
<td>Wet(MPa)</td>
<td>11.8</td>
<td>12.7</td>
<td>6.4</td>
</tr>
</tbody>
</table>

* phr : Parts per hundred resin (nonvolatiles)
Stability data of one packaging condition

Base resin: Acrylic copolymer on the market (Emulsion Acid value: 195 mgKOH/g nonvolatiles)
Storing condition: 50°C x One month after mixing
• Epocros shows longer pot life in comparison with that of water-soluble epoxies.
• Pot life can be longer when base resin is over neutralized

Improvement of Adhesion properties

• By adding Epocros, adhesion properties to various plastic substrates can be improved.
• The interaction between oxazine group and hydrophobic group on surface promotes adhesion properties. Furthermore, formation of covalent bond with carboxyl group on substrate surface results strong bonding.

Data of improving adhesion properties

Base resin: Chlorinated Polypropylene (Emulsion type, Acid value: 13 mgKOH/g, NV)
Substrate: Polypropylene test panel
Drying condition: 80°C x 30 min.
Evaluation method: Peel test with pressure sensitive adhesion tape (at room temperature)

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Amount of addition</th>
<th>Adhesion +/−</th>
<th>Water resistance of adhesion +/−</th>
</tr>
</thead>
<tbody>
<tr>
<td>No crosslinker</td>
<td>0%</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>K-2030E</td>
<td>10%</td>
<td>+</td>
<td>+/−</td>
</tr>
<tr>
<td>WS-500</td>
<td>3%</td>
<td>+</td>
<td>+/−</td>
</tr>
<tr>
<td>Water soluble epoxy</td>
<td>3%</td>
<td>+/−</td>
<td>−</td>
</tr>
</tbody>
</table>

+ : No peeling
+ / − : Partly peeled
− : Peeled almost entirely
− − : Entirely peeled
*1 1 at room temperature
*2 2 at room temperature after immersed in water for one day

Data of improving adhesion properties

Base resin: Acrylic copolymer (Emulsion type, Acid value: 39 mgKOH/g, Acryset EMN-260E(Nippon Shokubai Co., Ltd.))
Formulation: Crosslinkers are added to provide 0.5mol of each functional groups against carboxyl groups in the base resin.
Substrate: PP (Polypropylene)
ABS (Acrylonitrile - Butadiene - Styrene) resin
PC (Polycarbonate)
PMMA (Polymethylmethacrylate)
Drying condition: 150°C x one minute

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Amount of addition</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>No crosslinker</td>
<td>0%</td>
<td>PP</td>
</tr>
<tr>
<td>K-2030E</td>
<td>10%</td>
<td>−</td>
</tr>
<tr>
<td>WS-500</td>
<td>3%</td>
<td>−</td>
</tr>
<tr>
<td>WS-700</td>
<td>3%</td>
<td>−</td>
</tr>
<tr>
<td>Water soluble epoxy</td>
<td>3%</td>
<td>−</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crosslinker</th>
<th>Amount of addition</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>No crosslinker</td>
<td>0%</td>
<td>PP</td>
</tr>
<tr>
<td>K-2030E</td>
<td>5%</td>
<td>−</td>
</tr>
<tr>
<td>Water soluble epoxy</td>
<td>3%</td>
<td>−</td>
</tr>
</tbody>
</table>

+ : No peeling
+ / − : Partly peeled
− : Peeled almost entirely
− − : Entirely peeled

*1 1 at room temperature
*2 2 at room temperature after immersed in water for one day
EPCROS RPS-1005

Epcros RPS-1005 is an amorphia type reactive polymer which has oxazoline groups as its pendant. By utilizing the characteristics of oxazoline groups as polar functional groups and high reactivity they have with carboxyl groups, Epcros is expected to have wide variety of application fields in thermoplastic area as compatibilizer and dispersing agent.

### Imaginary diagram

- **polymer A**
- **polymer B**

< Boundary face > Micro Domain structure : Matrix (Polymer A) Domain (Polymer B)

### Characteristics

1. Oxazoline groups have high reactivity with carboxyl groups. Being melted and kneaded with melt polymers with carboxyl groups, they can quickly generate graft polymers.  
2. It has highly stable viscosity when melted and kneaded under high temperature.  
3. Customers can utilize polarity and ionic interaction arisen from oxazoline groups.

### Examples of uses

- **Compatibilizer**
  - By utilizing the reactivity of the oxazoline groups, Epcros can realize micro dispersion of dispersing phase as well as improving physical characteristics of moldings (especially improvement on impact strength).
- **Auxiliary agent for dispersing**
- **Epoxys can improve the dispersing status of pigments, fire retardants and bulking agents which are added into thermoplastic resins.**
- **Acid trapping agent**
- **Epoxys can improve heat stability of the moldings by trapping free acids generated in thermoplastic resins.**
- **Polymer chain extending agent**
- **Epoxys can improve viscosity of melting resins by introducing branch structure using oxazoline groups as the reactive sites.**
- **Extruded laminated body**
- **Laminated structure and laminated films can be generated without inserting adhesive layers between each layer by utilizing the reactivity between oxazoline groups and carboxyl groups contained in thermoplastic resins (ex. PET and / or Acid altered polyolefin)**

### Physical property basics of RPS-1005

#### Structural formula

```
(H=C(CH)₃)n
```

#### Properties

<table>
<thead>
<tr>
<th>Items</th>
<th>Property</th>
<th>Unit</th>
<th>Testing method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main structure</td>
<td>Styrene</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Appearance</td>
<td>White granule</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Density</td>
<td>1.05 g/cm³</td>
<td></td>
<td>JIS7112(B)</td>
</tr>
<tr>
<td>Amount of Oxazoline groups</td>
<td>0.27 mmol/g solid</td>
<td></td>
<td>Calculated Value</td>
</tr>
<tr>
<td>Molecular weight</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>Approx. 70,000 g/mol</td>
<td></td>
<td>GPC (Corresponding value to standard polystyrene)</td>
</tr>
<tr>
<td>Mw</td>
<td>Approx. 160,000 g/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass transition temperature</td>
<td>109 °C</td>
<td></td>
<td>DSC method</td>
</tr>
<tr>
<td>Thermal decomposition</td>
<td>403 °C</td>
<td></td>
<td>TG-DTA method weight decreasing temperature (measured under Nitrogen atmosphere)</td>
</tr>
<tr>
<td>temperature</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt flow rate (MFR)</td>
<td>6-10 g/10min</td>
<td>200°C, load 5Kg</td>
<td></td>
</tr>
</tbody>
</table>

Figures shown in the above table are representative values; these are not to be considered product specifications.

### Regulations

<table>
<thead>
<tr>
<th>CAS No.</th>
<th>Registering status</th>
</tr>
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<tbody>
<tr>
<td>30174-74-4</td>
<td></td>
</tr>
<tr>
<td>Law concerning the Examination and Regulation of Manufacture, etc. of Chemical substances</td>
<td>6-1961</td>
</tr>
<tr>
<td>TSCA [USA]</td>
<td>Registered</td>
</tr>
<tr>
<td>REACH [EU]</td>
<td>Not Registered</td>
</tr>
<tr>
<td>AREC (K-REACH) [KOREA]</td>
<td>Phase in substance</td>
</tr>
<tr>
<td>IECSC [CHINA]</td>
<td>Registered</td>
</tr>
<tr>
<td>Industrial Safety and Health Law</td>
<td>9-650</td>
</tr>
<tr>
<td>Fire Service Law</td>
<td>Nominated as a flammable material, synthetic resin</td>
</tr>
</tbody>
</table>