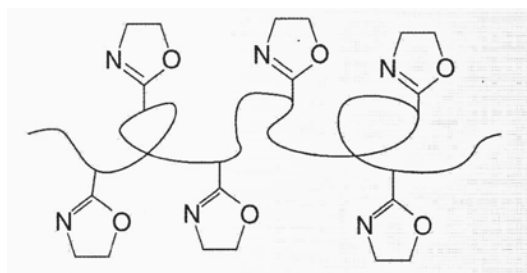


APR-200 ,500 Series (Oxazoline functional crosslinking agent)

APR 200 & 500 Series are unique polymer emulsions / solution containing pendant oxazoline groups designed to work as an effective waterborne crosslinking agent for polymer emulsions containing carboxyl functionality. The APR 200 & 500 Series resins demonstrate excellent adhesion to polyester and other substrates due to the oxazoline groups.



Features

- Low-Temperature Curing
- Long Pot-Life
- VOC Free (APR-200 series)
- Excellent Adhesion
- Excellent Water Resistance
- Low toxicity
- Adjustable Softness / Hardness

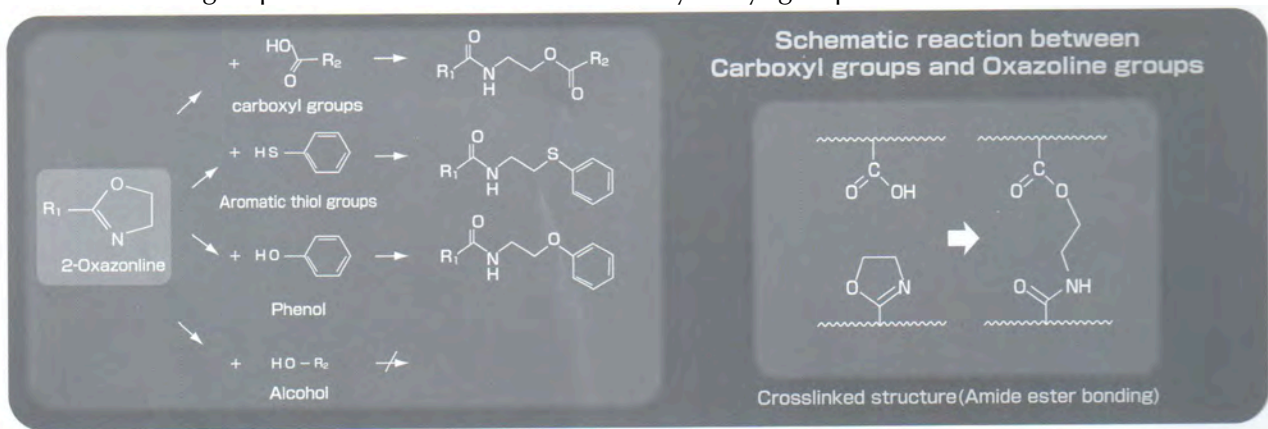
Applications

- Paints & Coating
- Adhesives
- Pressure Sensitive Adhesives
- Nonwoven Fabric Binders
- Inks
- Textile Treatment

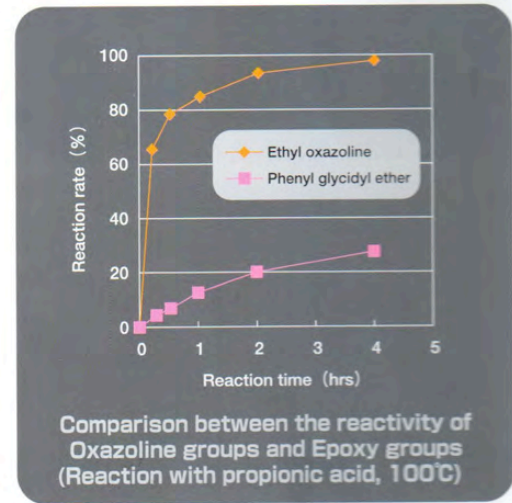
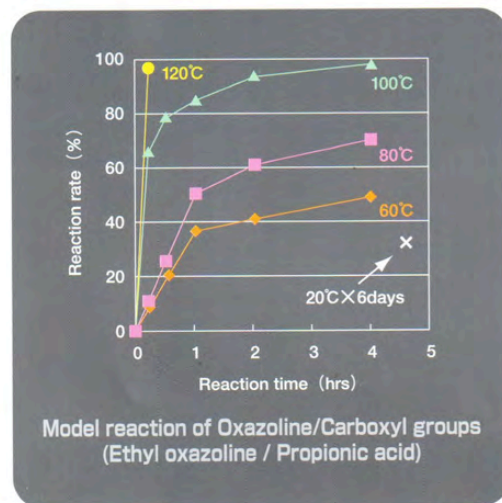
	APR-201	APR-202	APR-203	APR-500
Appearance	Milky-White Emulsion			Clear yellow liquid
Solid Content (%)	40 ± 1			39± 1
pH	7 – 9			8-10
Main Components	Styrene / Acrylic			Acrylic
T _g	-50°C(-58°F)	0°C(32°F)	50°C(122°F)	50°C(122°F)
Functional Group Equivalent (grams of solid/equivalent)	550			220
Oxazoline value	1.8			4.5
Solvent	Water			Water/1-methoxy-2-propanol

Reactivity

- Reaction with carboxyl groups is regarded to have the highest reactivity among other functional groups, after the reaction with the carboxyl groups; stable amid ester bonding is formed. And there will be no by-product generated.
- Reaction with carboxyl group proceeds rapidly at elevated temperature 80°C-100 °C, although reaction with carboxyl proceeds slowly at room temperature.
- Oxazoline groups also react with epoxy, aromatics such as thiol group, phenol groups however oxazoline groups will not react with alcoholic hydroxyl groups



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



Condition:

Ethyl oxazoline / Propionic acid = 1: 1 (mol/mol) solvent free reaction

Phenyl glycidyl ether / Propionic acid: 1: 1 (mol/mol) solvent free reaction

Method of analysis: Gas chromatography analysis

General Formulating consideration.

In theory, optimum addition level of APR series as cross linker is 1: 1 ratio to COOH mol amount. However under the effects of reacting conditions as well as the effect of other additives, between 0.2 to 1.0 ratio is considered to be recommended in actual usages.

	APR-200 Series	APR-500
Amount of Oxazoline Group (mmol/g, NV)	1.8	4.5
Non Volatile (N.V.)	40%	39%

<How to calculate addition level>

$$\text{Amount of APR series (g)} = \frac{(\text{Weight of base resin} \times \text{NV\% of base resin}) \times \text{COOH mol amount (m mol per g, NV)}}{(\text{NV\% of APR}) \times (\text{amount of Oxazoline group (mmol per g, NV)})}$$

$$\text{COOH mol amount (m mol per g, NV)} = \frac{\text{Acid value}}{56.1 (\text{KOH} : \text{g, mol})}$$

(EXAMPLE)

Acrylic resin (total weight 100g : solid 40%, acid value: 30 (mg KOH per g N.V.))

$$\text{COOH mol amount (m mol per g, NV)} = \frac{30}{56.1 (\text{KOH} : \text{g, mol})} = 0.53$$

$$\text{Amount of APR 200 series (g)} = \frac{(100\text{g} \times 40\% \times 0.53)}{(40\%) \times (1.8(\text{mmol per g, NV}))} = 29.4\text{g}$$

$$\text{Amount of APR 500 (g)} = \frac{(100\text{g} \times 40\% \times 0.53)}{(39\%) \times (4.5(\text{mmol per g, NV}))} = 12.1\text{g}$$

Amount needed to crosslink with Acrylic resin

	APR-200 series	APR-500
20mol%	5.9g	2.4g
100mol %	29.4g	12.1g

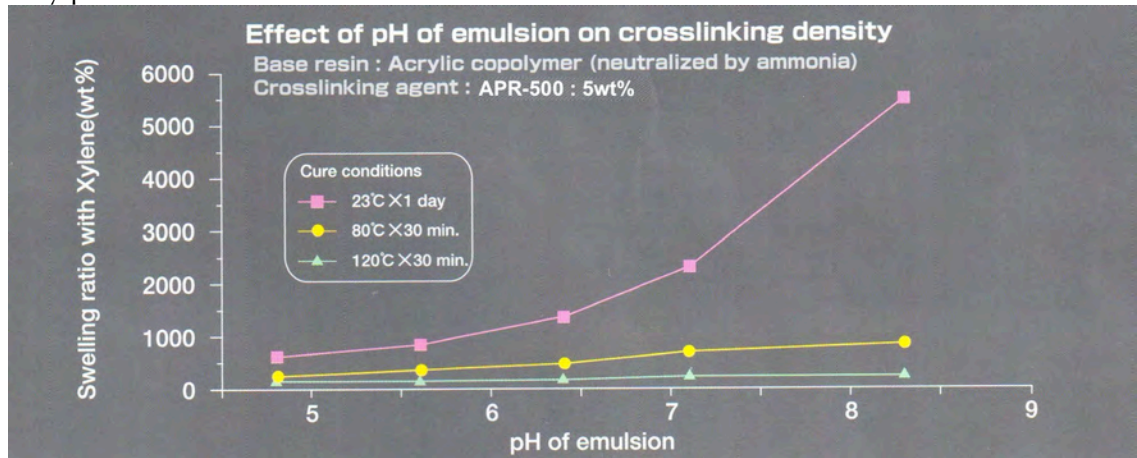
Effect of the neutralization agent on reactivity

Since the oxazoline group does not react with neutralized-carboxyl group, the formulation of APR-200 series / APR-500 and water-borne polymer containing neutralized carboxyl group generally has a long pot-life. If the neutralizing agent vaporizes during the process of drying, then the curing reaction proceeds. High-volatile neutralizing agent such as ammonia is recommended for low temperature curing.

(Effect of pH)

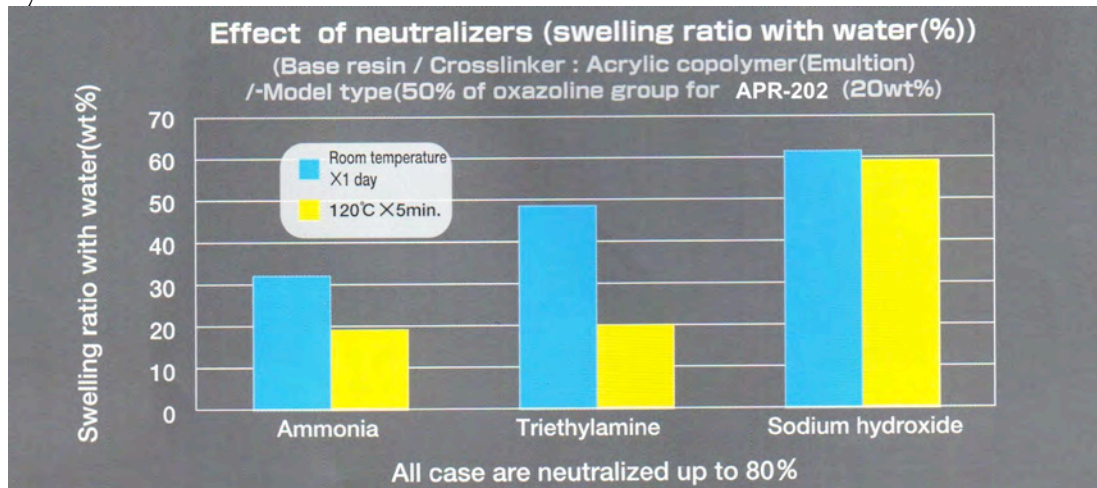
- Crosslinking density is inversely related to swelling ratio, As ammonia neutralizers have high evaporation rate, it is rarely affected by pH at elevated temperature (over 80 °C)

- At room temperature (20 °C), as ammonia neutralizer can not evaporate fast enough, it is highly affected by pH



(Effect of type of neutralizer)

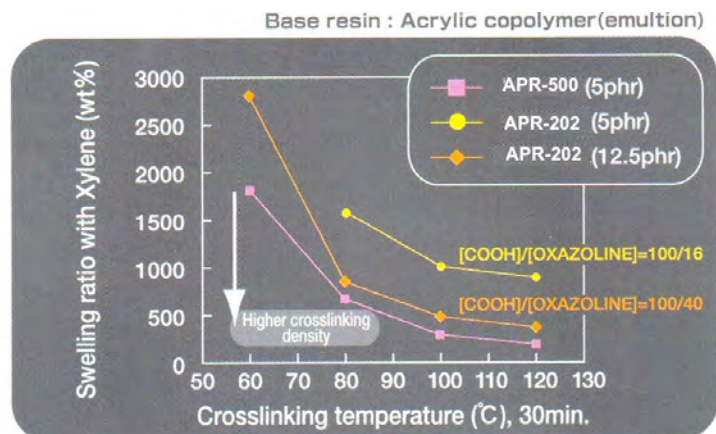
- Reactivity of APR series is affected by evaporation of neutralizer
- At elevated temperature (120 °C), neutralization by ammonia and triethylamine has similar reactivity.



Reactivity

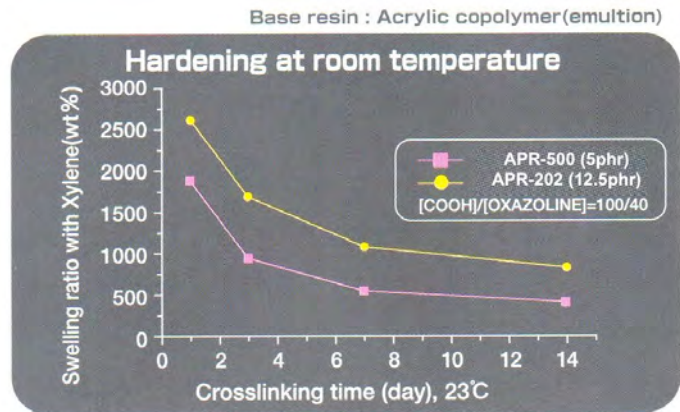
(Curing temperature)

- Hardening performance is significantly increased at 80°C and above.
- APR-500 demonstrated better hardening performance than APR-202 when the same amount was added



(Room temperature curing)

- It can be hardened under the room temperature, however significantly long curing time is required to get enough performance.
- APR-500 demonstrated better hardening performance than APR-202 when the same amount was added

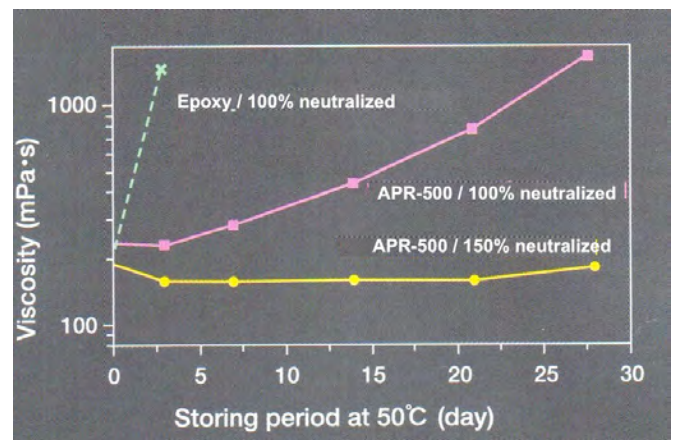


Reaction mechanism of storage stability

- The mixture of carboxylated resin and APR shows excellent storage stability under ambient conditions. This is attributed to blocking effect of neutralizers.
- As the neutralizer volatiles for example during the drying process, the reaction is accelerated.
- The product can be prepared as 1K system

Stability Data

- Base resin Acrylic copolymer (Acid Value; 195mgKOH/g NV)
- Storing condition 50°C x one month after mixing
- APR shows longer pot life than water-soluble epoxide.
- Pot life can be longer when base resins in over neutralized.



General Crosslinking agent comparison

	APR-200 /500Series	Aziridine	Water Soluble Epoxy	Water Soluble Melamine
Curing Temp	Medium/High	Low	Medium/High	High
Pot-Life	Long	Short	Short	Short
Toxicity	Low	High	High	High
Crosslink Density	Medium	High	High	Low

Performance result

a) Adhesion to various type of plastic substrate

- Base Resin: Acrylic copolymer (emulsion, acid value: 39mgKOH/g, NV)
- Formulation: Crosslinkers are added to provide 0.5mol of each functional group against COOH group in the base resin.
- Curing conditions: 150⁰C x 1 minute
- Evaluation: Peel test with pressure sensitive adhesion tape (room temp.)

Results:

Crosslinker	Addition	Substrate			
		PP	ABS	PC	PMMA
APR-500	8%	Peeled almost entirely	No peeling	No peeling	No peeling
Water soluble epoxy	6%	Peeled almost entirely	Peeled almost entirely	Peeled almost entirely	No peeling
Control	0%	Peeled almost entirely	Peeled almost entirely	No peeling	No peeling

b) Adhesion to PET film

- Base Resin: Acrylic copolymer (emulsion, acid value: 26mgKOH/g NV)
- Substrate: PET film (100um)
- Curing conditions: 150⁰C x 1 minute
- Evaluation: Peel test with pressure sensitive adhesion tape (room temp.)
- Water resistance: at room temperature after immersed in water for one day

Results:

Crosslinker	Addition	Adhesion	Water resistance
APR-202	5%	No peeling	Partly peeled
Water soluble melamine	3%	Peeled almost entirely	Entirely peeled
Water soluble epoxy	3%	Partly peeled	Peeled almost entirely
Control	0%	Peeled almost entirely	Entirely peeled