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COATINGS, ADHESIVES, SEALANTS, & ELASTOMERS

Denacol™ EX-622 and EX-614B Aliphatic Glycidyl Ethers

Ambient Crosslinkers with Acid-Functional Acrylics for High Performance NISO Coating Formulations

Nagase ChemteX

NAGASE Group

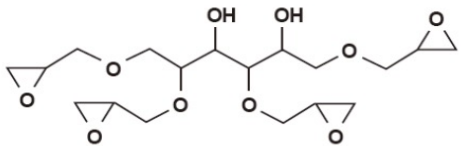
Introduction

Market development and interest in Non-Isocyanate ("NISO") coatings has increased over the past few years due to the health and safety concerns associated with isocyanates. Use of isocyanates in spray coatings can cause allergic skin reactions and irritation of the respiratory system in workers, and the risks need to be mitigated by using expensive personal protection equipment and training.

Challenges persist, though, in meeting required performance standards in a variety of applications. Nagase Specialty Materials NA LLC set out to develop preliminary formulations using a specific subset of the Denacol™ aliphatic epoxy product line as ambient crosslinking agents in NISO coatings used in outdoor applications which require a high degree of weather resistance. To assist with the study, Nagase partnered with ChemQuest Technology Institute: an independent, state-of-the-art coatings and adhesives application, formulation, and testing facility. Panels made using these preliminary formulations were then put through a battery of optical, physical, and chemical tests. Suitability of formulations to specific market applications based on results and possible areas of improvement to the preliminary formulations were reviewed.

Background

The Denacol EX-600 series, manufactured by Nagase ChemteX Corporation, is comprised of aliphatic tetrafunctional glycidyl ethers based on the epoxidation of bio-based sorbitol, as shown in the structure pictured to the right.



Two grades of Denacol were included in this study; one suitable for solventborne formulations (EX-622) and another for waterborne formulations (EX-614B). Each will act as an ambient temperature crosslinker to the defined resin.

Table 1

Denacol Product	Epoxy Equivalent (g/eq)	Water Solubility Rate (%)	Viscosity (mPa*s)
EX-622	191	Insoluble	11,800
EX-614B	173	94%	5,000

Commercially available acid-functional acrylics were selected for the resin. The solventborne system contained a high-solids resin to allow for low VOC formulations. The waterborne system contained an aqueous acrylic copolymer that allowed for long pot life and quick dry times.

The resulting preliminary formulations were evaluated as either the topcoat in a multi-layered coating system (with varying combination of Zinc-Rich Primer/Epoxy Intermediate/Top Coat) or Direct To Metal (DTM). Cold rolled steel (CRS) or blasted CRS panels were used, except for humidity and Xenon testing, which were done with aluminum panels. Coatings were applied using an HVLP spray gun (2.4 mm nozzle, 40 PSI). 7 days of ambient temperature cure were allowed before testing commenced.

Table 2

	Organic zinc rich primer (ZRP)	Epoxy intermediate coat (IM)
	Zinc clad 4	**Macropoxy 646**
Volume solids (data sheet):	68.0%	72.0%
VOC (g/l) (data sheet):	340.0	250.0

- ZRP – 3.5 mils (on average)
- Top Coat (TC) - DTM – 3 mils (on average)
- IM/TC - 7 mils (on average)
- ZRP/IM/TC – 11.5 mils (on average)
- ZRP/TC – 6 mils (on average)

Formulation Details

Table 3: Acrylic/Aliphatic Epoxy (NISO) - Solventborne

Weight Solids (Calculated):	77.60%
Volume Solids (Calculated):	69.50%
VOC (g/L)(Calculated):	265.9
Part A	
Acid Functional Acrylic Resin, SB	704.8
Anti-Terra-204 (Dispersant)	1.4
Bentone SD-1	3.6
TiO2 (R-706)	135.0
SZP-391 (Corrosion Inhibitor)	54.0
Xylene	9.0
Part B	
Denacol EX-622	90.0

Table 4: Acrylic/Aliphatic epoxy (NISO) - Waterborne

Weight Solids (Calculated):	56.00%
Volume Solids (Calculated):	44.40%
VOC (g/L)(Calculated):	72.7
Part A	
Water	74.5
Ammonia	2.7
Tamol 1124 (Dispersant)	6.8
Triton CF-10 (Surfactant)	2.2
Tego Foamex 1488	3.1
TiO2 (R-706)	179.6
Aqueous Acrylic Copolymer	584.5
Acrysol I-62A (Thickener)	4.5
Acrysol RM-12W (Thickener)	1.3
Texanol (Coalescent)	26.9
Water	13.5
SZP-391 (Corrosion Inhibitor)	53.9
Part B	
Denacol EX-614B	89.8

Performance Results

Test on Liquid and Cured Coatings (DTM, blasted CRS unless otherwise noted):

Table 5

	NISO Solventborne	NISO Waterborne
Cross Hatch Adhesion (ASTM D-3359)		
Cold Rolled Steel (CRS) - DTM	0	5
Blasted CRS (B-CRS)- DTM	5	5
B-CRS (IM/Top Coat)	5	5
B-CRS (ZRP/IM/TC)	4	2
B-CRS (ZRP/TC)	4	5
Pencil Hardness (ASTM D-3363)	F	F
Flexibility	1/8"	1/8"
Forward Impact (lbs)	20	80 +
Reverse Impact (lbs)	0	80 +
Gel Time (min)	92	3,484
Dry Time (hrs)	14	1

Table 6: Chemical Resistance

	Spot tests								Immersion
	10 Minutes		24 Hours				7 Days		5 minutes, 15 minutes air dry (Repeat 5X)
Material	Gasoline	Xylene	Diesel	Oil	1% NaOH	DI Water	37% H 2SO4	50% NaOH	Gasoline
NISO Solventborne	R,S	B,S,R	R	N	R	R	R,LG	R,S,IG	S, C
NISO Waterborne	R,S	R,S	N	N	B	B,CR	LG	R,IG	S

N-Nothing S-Softening LG-Loss of Gloss IG-Increase of Gloss B-Blister R-Ring Cr-Corrosion C=Cracking

Table 7: Optical Properties (Post Cure)

	NISO Solventborne	NISO Waterborne
20° Gloss	84.1	28.1
60° Gloss	91.4	61.7
L*	94.6	95.1
a*	-1.2	-1
b*	0.9	0.5
OPACITY	94.3	88.3

Table 8: Corrosion Resistance (DTM, 2,500 hours)

Type	Blistering	Creep at Scribe	Rust-Thru (0-4, 0=None, 4=Major)
NISO Solventborne	4M	0	3

Note: NISO Waterborne preliminary formulation panels experienced significant corrosion prior to testing completion.

Table 9: Humidity Resistance (ASTM D714, DTM, 1,000 hours)

	First Failure (Hours)	First Failure (ASTM Rating)	1000 hours (ASTM Rating)
NISO Solventborne	24	4D	2D
NISO Waterborne	24	6F	6MD

Table 10: Xenon Exposure (DTM, 2,000 hours)

20° Gloss White

Hours	0	24	100	250	500	750	1000	1250	1500	2000
NISO Solventborne	83.0	85.0	73.6	69.8	66.7	59.9	60.0	55.8	57.9	47.2
NISO Waterborne	25.3	14.7	13.6	13.9	15.2	12.5	14.2	14.2	15.3	13.9

60° Gloss White

Hours	0	24	100	250	500	750	1000	1250	1500	2000
NISO Solventborne	92.2	92.5	90.0	88.6	87.7	83.9	83.7	82.4	82.9	78.1
NISO Waterborne	66.8	48.6	49.3	50.1	52.7	48.2	50.4	50.2	52.3	50.4

Delta E White

Hours	0	24	100	250	500	750	1000	1250	1500	2000
NISO Solventborne	0.0	0.4	0.6	0.7	0.6	0.8	0.8	0.8	0.8	0.8
NISO Waterborne	0.0	0.4	0.6	0.5	0.5	0.7	0.6	0.5	0.5	0.5

Recommendations

NISO Solventborne Formulation

- The NISO SB preliminary formulation, utilizing Denacol EX-622 as an ambient crosslinker, displayed good weatherability (gloss retention and yellowing resistance) and corrosion resistance. Its impact resistance and hardness are particularly notable when compared to existing commercial NISO technologies.
- These attributes are a fit for the following applications:
  - Factory and shop applied coatings meant for exterior applications
    - NISO coatings reduce risks to worker health
  - Agricultural, construction, and earth moving equipment
  - Railcars
  - Outdoor water tanks
- Formulation refinement:
  - Improved pot-life and dry time
    - Examine usage of alternative acid functional acrylic resins, with a focus on lower acid numbers/higher Mw and/or higher MFFT
  - Improved corrosion resistance
    - Examine use of supplemental corrosion resistance enhancers and or adjusting additive amounts

NISO Waterborne Formulation

- The NISO WB preliminary formulation, utilizing Denacol EX-614B as an ambient crosslinker, displayed excellent pot-life and dry time. Its impact resistance was even greater than that of the SB formulation.
- The corrosion resistance and gloss performance may be improved by investigating the following areas of refinement:
  - Improved corrosion resistance
    - Examine use of supplemental corrosion resistance enhancers and or adjusting additive amounts
  - Improved optical/gloss properties
    - Examine use of small quantities of water-soluble polar solvents in addition to the Texanol to improve coalescence

Conclusions

Due to the worker health risks associated with using isocyanate-based coatings in spray application settings, NISO-based coating interest has continued to grow. There are challenges in developing alternatives that meet the performance requirements for a variety of different industry applications. Nagase Specialty Materials NA LLC has developed two different preliminary NISO coating formulations to address these challenges, using the Denacol line of aliphatic epoxies manufactured in commercial volumes by our subsidiary company Nagase ChemteX. These formulations were then evaluated according to a variety of industry standard tests to provide the best foundation of information for future developmental refinement. The Denacol tetrafunctional glycidyl ethers, when used in conjunction with acid functional acrylic resins, prove to be an effective ambient crosslinker resulting in NISO coatings with good weatherability, impact resistance, and hardness.

To learn more about the Denacol line please visit our website at nagase.com.