General Introduction and Some Advances on Denka Neoprene® Latex for Adhesive Applications

Dr. Mousumi De Sarkar
Content

- Introduction to Denka Group & Denka Chloroprene Rubber Business
- Basics of Chloroprene Rubber
- Introduction to Denka Neoprene® Liquid Dispersion (LD) → Commercial Grades for Adhesive Applications
- New Developments in Denka Neoprene® LD → Specialty Adhesive Applications
Introduction to Denka Group & Denka Chloroprene Rubber Business
Possibility of chemistry......

Facts

- **Established**: May, 1915
- **Net Sales**: ~ ¥ 363 billion yen (Fiscal Year 2016)
- **Employees** (Consolidated) ~ 5,816 (as of March 2017)
- **Headquarter**: Tokyo, Japan
- **Production Facilities**: Japan, USA, Singapore, Vietnam, Malaysia and China.

Pioneer in Japanese Chemical Industry
Key Business Segments of DENKA Group

- **Elastomers & Performance Plastics**
  - Macromolecular chemical products business
  - Chloroprene rubber, Ethylene Acrylate Rubber (ER), Styrene monomer & Resins, Acetyl chemicals

- **Infrastructure & Social Solutions**
  - Focused on agri. & infrastructural applications, leveraging primarily inorganic chemistry
  - Cement, special cement additives, fertilizers, inorganic chemicals & plastic products

- **Electronics & Innovative Products**
  - Focused on advanced materials leveraging inorganic, organic, & macromolecular chemistry
  - Electronic packaging materials, functional ceramics, circuit substrates, heat-dissipation materials, adhesives, etc.

- **Living & Environ. Products**
  - Focused on enhancing quality of life & betterment of living environment
  - Plastic products for industrial packaging, household applications etc.

- **Life Innovation**
  - Focused on prevention & screening of deceases & services to provide diagnostic info.
  - Medical science products i.e. vaccines, diagnostic reagents, sodium hyaluronate etc
Denka Chloroprene Rubber Business

Denka Performance Elastomer: *Denka Neoprene*®

- **1931** - EI DuPont marketed DuPrene® → 1st synthetic rubber
- **1937** - DuPont changed DuPrene® to Neoprene®
- **1965** - Butadiene Process Technology Introduced for Production
- **2015** - Denka Acquired the DuPont’s Neoprene Business

**DENKA CR**

- **1962** - Denka Developed Chloroprene rubber production using Acetylene Technology
- **2009** - Capacity Expansion to 100,000 MT/Year
- World’s Largest Producer of Chloroprene rubber with over 100 Grades
Denka Chloroprene Rubber Business: *Leading Globally*

- Denka Chloroprene: Market Leader Globally
- Extensive & Diversified Portfolio of Quality Products

<table>
<thead>
<tr>
<th></th>
<th>Denka Neoprene®</th>
<th>Denka CR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technology</td>
<td>Butadiene</td>
<td>Acetylene</td>
</tr>
<tr>
<td>Production Site</td>
<td>Pontchartrain, LA, USA</td>
<td>Omi, JAPAN</td>
</tr>
<tr>
<td>Primary Market Focus</td>
<td>The Americas (North, South &amp; Central America)</td>
<td>Asia Pacific, Europe</td>
</tr>
</tbody>
</table>
Basics of Chloroprene Rubber
Introduction to Chloroprene Rubber

Structure similar to NR
- Flex Resistance
- Strain Crystallization
- Abrasion resistance

Cl instead of CH₃
- Oil Resistance
- Resistance of Oxidation, Aging, Ozone
- Low Flammability
- Enhanced cohesive strength & wettability

Specific Gravity (Polymer): 1.23
Adhesion to Metals/ Fabrics: Excellent
Permeability to Gasses: Low
Flame Resistance : Excellent
Resistance to Environmental Factors
- Ozone: Good
- Sunlight: Very Good
- Heat Aging : 100 °C in continuous service (120 °C intermittent)
- Low Temperature : ~ -40 °C (No Plasticizer) ~ -60 °C (With Plasticizer)

8/9/2017
Production of Denka Chloroprene: Basic Chemistry

Neoprene® Process

Butadiene

+ Cl₂ (Chlorination)

1-4 Di chloro 2- butene

Isomerization

3-4 Dichloro 1 butene

Chloroprene Monomer

Denka CR Process

CaCO₃ → CaO → CaC₂ → C₂H₂ → ChCl=CH=CH₂ → Chloroprene Monomer

+Cl₂ (Chlorination)

CaO + C + H₂O → CaC₂ → C₂H₂ → CHCl=CH=CH₂ → Chloroprene Monomer

Electrolysis

NaCl → HCl → Hydrochloric Acid → Chloroprene Monomer
Production of Denka Chloroprene: **Emulsion Polymerization & Finishing**

**Steps:**
1. Chloroprene Emulsifiers Additives
2. Monomer Solution
3. Water Solution (Water Caustic)
4. Emulsification
5. Polymerization
6. Catalyst Stabilizer
7. Stripping
8. Freeze Roll
9. Washing Drying
10. Rope Cutter
11. Latex
12. Dry Neoprene®
Introduction to Denka Neoprene® Liquid Dispersion (LD) → Existing Grades for Adhesive Applications
Denka Neoprene® Liquid Dispersion (LD)

- Produced through emulsion polymerization
- Nominal Solid Content ~ 50 to 60%
- Average rubber particle sizes ranging between 140 to 210 nm.
- Neoprene® LD commercial grades are available as Anionic Surfactant system
- All commercial grades are GEL Types: With varying degrees of Gel (~85-97%)
Denka Neoprene® Liquid Dispersion (LD)

Inherent Properties:
• Excellent film formation
• High cohesive strength even without curing
• Elastomeric properties over wide temperature range
• Considerable resistance to degradation from flame, weather, ozone, heat, water & many oils and chemicals

Typical Applications:
• Water-borne Adhesives: Pressure sensitive, Heat/ solvent activated for Laminating and Contact Bond; Mastics etc.
• Binders: As solvent and wet-end additives for fibrous products e.g. paper, non-woven, bonded batts etc.
• Coatings: Industrial and decorative
• Dipped Goods: Supported and unsupported films
• Elasticized asphalt
• Foam
## Elastomeric Adhesives: Where does Neoprene® Stand?

<table>
<thead>
<tr>
<th></th>
<th>Strength</th>
<th>Dead Load</th>
<th>Tack</th>
<th>Resistance to</th>
<th>Water</th>
<th>Oil</th>
<th>Gasoline</th>
<th>Heat</th>
<th>Cold</th>
<th>Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrile (NBR)</td>
<td>E</td>
<td>F</td>
<td>P-G</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>Butyl (IIR)</td>
<td>F</td>
<td>P</td>
<td>G</td>
<td>E</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>F</td>
<td>G</td>
<td>E</td>
</tr>
<tr>
<td>SBR</td>
<td>F</td>
<td>P</td>
<td>F</td>
<td>E</td>
<td>P</td>
<td>P</td>
<td>F</td>
<td>G</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>Natural (NR)</td>
<td>G</td>
<td>P</td>
<td>E</td>
<td>E</td>
<td>P</td>
<td>P</td>
<td>P</td>
<td>G</td>
<td>F</td>
<td>F</td>
</tr>
<tr>
<td>Neoprene®</td>
<td>E</td>
<td>G</td>
<td>P-G</td>
<td>E</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G-E</td>
<td></td>
</tr>
</tbody>
</table>

**E** = Excellent, **G** = Good, **F** = Fair, **P** = Poor

**Neoprene®**: One of the most versatile materials used as a base for Adhesives....
Denka Neoprene® Liquid Dispersion (LD) for Adhesives Appln

- Adhesive
  - Adhesive Strength
    - Increases by:
      - High Polarity
      - Low Molecular wt → **Low Gel**
  - Cohesive Strength
    - Increases by:
      - High Molecular Wt. → **High Gel**
      - High Crystallization

Neoprene® LD Grades

- Key Variants
  - A. Rate of Crystallization
  - B. Gel Content
A. Crystallization of Neoprene®: Effect of Microstructure

1,4 trans → Stereo Regular Structure → Primary Reason for Crystallization
     → Higher Level of trans-=> Faster crystallization)

1,4 –trans (~85%)

1,2 vinyl (~1.5%)

1, 4- cis (~10%)

3,4 vinyl (~1%)
A. Crystallization of Neoprene®: Technology to Control

Rate of Crystallization can be Controlled by

1. Polymerization Temperature (Lower polymerization temperature → Faster crystallization)

2. Incorporation of Co-monomer* in the polymer chain (More → Slower crystallization)

- Copolymerization disrupts the regularity of the Neoprene® polymer chain and thereby retards the rate of formation of crystallites in the polymer matrix. Crystallization of the polymer is thus prevented.

*2-3-dichloro 1,3 butadiene
B. Crystallization of Neoprene®: Effect on Adhesive Prop.

Crystallization of Polychloroprene: An unique features among elastomer based adhesives

With Increase in Crystallization

* Setting Rate
* Cohesive Strength at Room Temp.
* Water Resistance
* Hardness/ tensile

* Dry Contactability
* Tack & building tack
* Oil swell
* Extensibility
B. Gel Content in Neoprene®: Effect on Adhesive Properties

As Gel Content Increases

- Cohesive strength
- Hot-bond strength
- Heat resistance
- Hardness/ Tensile/ Modulus

- Contactability <--Polarity
- Adhesive strength
- Dry tack
- Oil swell
- Elongation
<table>
<thead>
<tr>
<th>Main Feature</th>
<th>571</th>
<th>671A</th>
<th>750</th>
<th>842A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Solid Content (%)</td>
<td>50</td>
<td>59</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Initial pH at 20 °C</td>
<td>13</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Brookfield Viscosity at 25 °C, 30 rpm; cps</td>
<td>13</td>
<td>40</td>
<td>15</td>
<td>13</td>
</tr>
<tr>
<td>Crystallization Rate (Relative)</td>
<td>Rapid</td>
<td>Moderate</td>
<td>Slowest</td>
<td>Slow</td>
</tr>
<tr>
<td>Gel Content</td>
<td>High</td>
<td>Med-High</td>
<td>Med-High</td>
<td>High</td>
</tr>
<tr>
<td>Cure Rate</td>
<td>Slow</td>
<td>Med-High</td>
<td>Medium</td>
<td>Fast</td>
</tr>
<tr>
<td>Typical Adhesive Application: Example</td>
<td>Shoe assembly, Gaskets</td>
<td>- Contact Adhesive - Mastics/ sealants</td>
<td>Contact Adhesive</td>
<td>Foil-Paper Laminating Adhesive</td>
</tr>
</tbody>
</table>
### Compounding with Neoprene® Liquid Dispersions

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Primary Functions</th>
<th>Examples</th>
<th>Typical Level</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Antioxidant</strong></td>
<td>• Prevents oxidative degradation</td>
<td>Hindered bis-phenols</td>
<td>Typically 1 to 2 phr. Higher amount for severe service conditions</td>
</tr>
<tr>
<td><strong>Metal Oxides</strong></td>
<td>• Acts as acid acceptor</td>
<td>Mostly Zinc Oxide (typically incorporated as dispersion) MgO → not used in LDs</td>
<td>Typically 5 phr. Higher amount for sunlight/ high temperature exposures applications</td>
</tr>
<tr>
<td></td>
<td>• Improves resistance to aging/heat/light</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Promotes crosslink</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tackifier/Adhesion promoter</strong></td>
<td>• Increase adhesion</td>
<td>Resins (e.g. Terpene Phenolic resins), Acrylic emulsions, PVA etc.</td>
<td>10 to 100 phr</td>
</tr>
<tr>
<td></td>
<td>• Enhance tack</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Thickener</strong></td>
<td>• Controls viscosity</td>
<td>PolyaCRYlates, cellulose derivatives polysaccharides , NH₄⁺salt of proteins (e.g. ammonium caseinate) etc</td>
<td>0.5 to 3 phr (typically added as needed depending of viscosity requirement)</td>
</tr>
<tr>
<td></td>
<td>• Controls rheology</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Curatives</strong></td>
<td>• Increase cure rate</td>
<td>Thiocarbamate alone or in combo with DPG/DOTG</td>
<td>Normally 1 to 3 phr of each</td>
</tr>
<tr>
<td></td>
<td>• Enhance physical properties</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Others:** Fillers, stabilizers (e.g. freeze-thaw stabilizer), surfactants, antifoam agent, hardeners, colors/pigments, etc & other elastomers (NR, SBR, NBR etc) at blends
## Denka Neoprene® LD: Comparison of Adhesive Performance

### Effect of Level of Tackifier (Rosin Ester) with Neoprene LD 671A:

<table>
<thead>
<tr>
<th>Tackifier: Ester of tall oil rosin (phr)</th>
<th>25</th>
<th>50</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tack Life, hrs (Decorative laminate - chipboard under Roller press)</td>
<td>24</td>
<td>24</td>
<td>&lt; 6</td>
</tr>
<tr>
<td>Peel Strength, kN/m (Canvas-canvas, OT=1 hr, ST=1 wk)</td>
<td>4.1</td>
<td>2.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Creep at 23 °C, mm (3 kgs/ 2.5 cm/ 30 m)</td>
<td>2</td>
<td>7</td>
<td>15</td>
</tr>
<tr>
<td>Creep at 70 °C, mm (500 g/ 2.5 cm/ 30 m)</td>
<td>8</td>
<td>34</td>
<td>45</td>
</tr>
</tbody>
</table>

*Formulations compounded with ZnO and antioxidant*

### Effect of Types of LD Grades

<table>
<thead>
<tr>
<th>Neoprene LD Grade</th>
<th>571</th>
<th>671A</th>
<th>750</th>
<th>842A</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tackifier: Ester of tall oil rosin (phr)</td>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Tack Life, hrs (Decorative laminate - chipboard under Roller press)</td>
<td>&lt; 6</td>
<td>24</td>
<td>&lt; 6</td>
<td>3</td>
</tr>
<tr>
<td>Peel Strength, kN/m (Canvas-canvas, OT=1 hr, ST=1 wk)</td>
<td>2.2</td>
<td>4.1</td>
<td>3.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Creep at 23 °C, mm (3 kgs/ 2.5 cm/ 30 m)</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>Creep at 70 °C, mm (500 g/ 2.5 cm/ 30 m)</td>
<td>42</td>
<td>8</td>
<td>-</td>
<td>66</td>
</tr>
</tbody>
</table>

*Formulations compounded with ZnO and antioxidant*
New Developments in Denka Neoprene® LD → Specialty Adhesive Application
Denka Neoprene® New & Existing Grades: Mapping

![Diagram showing the mapping of Denka Neoprene® grades based on gel content and crystallization rate.]

- **Fast** Gel Content:
  - Low: DG-1
  - Medium: DG-2
  - High: 571

- **Slow** Gel Content:
  - Low: 750
  - Medium: 671A
  - High: 842A

- **Commercial Grades:**
  - 571

- **Developmental Grades:**
  - DG-1
**DG-1**: A Specialty Chloroprene for Fast-Tack Adhesives: PU Foam

**Formulation**: Neoprene®: 100, Plasticizer: 5, Glycine: 6

<table>
<thead>
<tr>
<th></th>
<th>New</th>
<th>Existing LDs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DG-1</td>
<td>671A</td>
</tr>
<tr>
<td>pH</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>Brookfield Viscosity mPa-sec, 25 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>× 6rpm</td>
<td>101</td>
<td>101</td>
</tr>
<tr>
<td>× 12rpm</td>
<td>102</td>
<td>102</td>
</tr>
<tr>
<td>× 30rpm</td>
<td>99</td>
<td>99</td>
</tr>
<tr>
<td>× 60rpm</td>
<td>92</td>
<td>92</td>
</tr>
<tr>
<td><strong>Adhesive Strength (N/cm²)</strong> PU Foam-PU Foam</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Open time 10sec</td>
<td>4.7</td>
<td>1.0</td>
</tr>
<tr>
<td>Open time 1min</td>
<td>5.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Open time 5min</td>
<td>6.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Open time 20min</td>
<td>3.9</td>
<td>1.2</td>
</tr>
</tbody>
</table>

**Unique Features of DG-1 (Development Grade)**:

- **Much faster rate of crystallization** → rapid rate of bond formation & high cohesive strength
- **Very Low Gel content** → flows more easily under pressure → desirable for “quick break” adhesive
- **Higher molecular weight** → superior ultimate bond strength

“Quick Break”

Formulation: Neoprene®: 100, Plasticizer: 5, Glycine: 6
**DG-2: A Specialty Chloroprene for Adhesives for Non-Polar Plastic Substrates**

**Technical Approach:**
- Specialty CR grade & Innovative formulation design for adhesives for PP substrate

**Unique Features of DG-2 (Development Grade):**
- Increased stability
- Medium Gel content → longer tack time
- Higher Viscosity and larger av. particle size (~350 nm)

<table>
<thead>
<tr>
<th></th>
<th>Ref</th>
<th>New-1</th>
<th>New-2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Neoprene® 750</strong></td>
<td>100</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td><strong>DG-2</strong></td>
<td>0</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td><strong>Proprietary Resin Emulsion</strong></td>
<td>0</td>
<td>0</td>
<td>15</td>
</tr>
</tbody>
</table>

**PP-Canvas Peel Strength, N/mm**

- Initial, RT (ST=10min): 0.1, 0.5, 0.8
- Final RT (ST=5 days): 0.3, 0.4, 0.8
- Final, 80 °C (ST=5 days): 1.0, 1.6, 1.6

**PP-Canvas Heat Creep, mm** [24 hrs, 100 g]

- At 80 °C: 35, 0, 0
- At 100 °C: Fail, 70, 0

Formulation also contain Tackifier: 50, ZnO: 1, Thickener: As required
Specialty Chloroprene for Adhesives for Non-Polar Plastic Substrates:

<table>
<thead>
<tr>
<th>Water-Borne Adhesive* (Optimized)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Neoprene® 750</td>
<td>50</td>
</tr>
<tr>
<td>DG-2</td>
<td>50</td>
</tr>
<tr>
<td>Proprietary Resin Emulsion</td>
<td>15</td>
</tr>
<tr>
<td><strong>PP-Canvas Peel Strength, N/mm</strong></td>
<td></td>
</tr>
<tr>
<td>Initial, RT (ST=10min)</td>
<td>0.8</td>
</tr>
<tr>
<td>Final RT (ST=5 days)</td>
<td>0.8</td>
</tr>
<tr>
<td>Hot Bond, 80 °C (ST=5 days)</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>PP-Canvas Heat Creep, mm</strong></td>
<td></td>
</tr>
<tr>
<td>At 80 °C</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solvent-Borne Adhesive (Optimized)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Denka CR®</td>
<td>100</td>
</tr>
<tr>
<td>Proprietary Resin Emulsion</td>
<td>10</td>
</tr>
<tr>
<td><strong>PP-Canvas Peel Strength, N/mm</strong></td>
<td></td>
</tr>
<tr>
<td>Initial, RT (ST=10min)</td>
<td>0.6</td>
</tr>
<tr>
<td>Final RT (ST=5 days)</td>
<td>0.9</td>
</tr>
<tr>
<td>Hot-bond, 80 °C (ST=5 days)</td>
<td>2.2</td>
</tr>
<tr>
<td><strong>PP-Canvas Heat Creep, mm</strong></td>
<td></td>
</tr>
<tr>
<td>At 80 °C</td>
<td>5</td>
</tr>
</tbody>
</table>

Formulation* contains Tackifier: 50, ZnO: 1, Thickener: as required to viscosity: of 3000-6000 mPa·s

Possible to Achieve Comparable Performance of Water-borne Adhesives & Solvent based Adhesives, when Formulated Specifically
Denka Neoprene® Business: *Poised for Growth*

Denka Neoprene® is a Core Business, Structured for Growth

- Global Experience for Several Decades
- Strong Research & Developmental Focus
- Extensive Technical Service Support
- Second Source Capability from Denka CR

**Denka Neoprene: A Reliable Partner for Adhesive Industries**

- Several Grades
- High Level of Customer Support
- Flexible Response of Customer/ Market Demands
Thank you for your kind attention.

Possibility of chemistry......