Light stabilizers and antioxidants
Principles of Light stabilizers
Degradation of polymers

- Oxygen
- Peroxides: alcohols, ketones, aldehydes, acids, peracids
- Energy: mechanical stress, heat, UV light
- Air pollution: NOx, SOx...
- Heavy metals: Metals/-ions
Consequence of polymer degradation

Loss of mechanical properties
Color change
Change in clarity
Surface chalking
Loss of gloss
Shortened service life
Crack
Intensity distribution of sunshine

- 0.7-280nm----- 0 %
- 280-400nm----UV light 6%
- 400-750nm----Visible light 52%
- 750-3000nm---Infred light 42%
Light stabilizers

• **UV absorbers**  
  provide a screening effect by competitively absorbing UV light

• **Quenchers**  
  deactivate the excited states of the chromophores

• **Free radical scavengers**  
  interrupt the auto-oxidation process by scavenging free radicals
UV absorber

- What is UV? UVC: below 280 nm (mainly screened by Ozone layer)
  UVB: 280-320 nm, UVA: 320-400 nm
- Benzotriazole
- Benzophenone
- Acrylate
- Reactable
- Others
• **KLY**

1 KLY = 1 Kcal/cm² · year

Florida approx. 140KLY /year

Arizona approx. 190KLY /year

Taiwan approx. 120-140KLY /year

• **AFU**
Rating of lightness

- AATCC & ISO method:
  Gray scale for colorchange & stain
  $\Delta E^*, L^*, a^*, b^*$
UV Absorber

- Benzophenone
  Chisorb BP-3, BP-12

*1.2 mg of BP-3 in 100 ml of Methanol
Chisorb

Benzophenone

- Chinox BP-1
- Chisorb BP-3
- Chisorb BP-4
- Chisorb BP-12
• Benzotriazoles

Chisorb P,
234,325,326,327,328,5103,5228S,5411,5431,5687
Chisorb

**Benzotriazole 1**

- Chisorb P
- Chisorb 320
- Chisorb 325
- Chisorb 326
- Chisorb 327
- Chisorb 328
Chisorb

Benzotriazole 2

- Chisorb 234
- Chisorb 5411
- Chisorb 5431
• **Others**: dialkylaminobenzoic ester
  Acrylate, Benzoate, Methoxycinnamate, Oxanilide ....
  Chisorb 335, 336, 971, 389, 1268, 5540...
Chisorb

**Acrylate**
- Chisorb 335
- Chisorb 336

**Others**
- Chisorb 1300, 1500 (anti-NOX, anti-gas fading)
- Chisorb 1268
- Chisor SUV
- Chisorb 2260
Performance of quenchers

- Environmentally unfriendly, contamination of soil
- Not popularly used now
- Slowly phase out from the market
HALS

• HALS general combined with UVA in most application

\[ \text{N-R} \stackrel{(O)}{\longrightarrow} \text{N-O}^\circ \]

\[ \text{N-O}^\circ + \text{R}^\circ \longrightarrow \text{N-O-R} \]

\[ \text{N-O-R} + \text{R'}\text{OO}^\circ \longrightarrow \text{ROOR'} + \text{N-O}^\circ \]
Hindered Amine Light Stabilizer

- **Monomer**

**Chisorb 770**

Liquid type

**Chisorb 292, 353**
Chisorb

- Chisorb 770
- Chisorb 292
- Chisorb 622
- Chisorb 944
- Chisorb 519 (anti-pesticide, acid rain)
Hindered Amine Light Stabilizer

- **Oligomer**
  
  Chisorb 622, 944, 519...

- **Chisorb 519**

  \[
  \text{R} = \text{N}(\text{CH}_2)_{6}\text{N} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
  \]

  \[
  \text{R} = \text{N} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
  \]
Chisorb

Reactable

- Chisorb 5687 (double bond remained)
- Chisorb 5103 (2-OH function)
Chisorb

Reactable

• Chisorb 5687
**Reactable UV absorber**

**Chisorb 5103**

**Benefit:**
- Good dispersion with high molecular weight, could be used as reactive UVA without migration
- Used as di-functional polyol in PU, polyester system reacted in back bond, possible for long term application and food contact application
**Water borne UV absorber**

**Chisorb 5228 S**

Benefit:

- Water soluble UVA, used for water borne system, and textile application improve light fastness, such like Nylon, silk, wool

![Chemical structure of Chisorb 5228 S]

**Chisorb SPF-1: emulsified UVA**

Benefit:

- Water soluble UVA, used for water borne system, and textile application improve light fastness
Weatherability of LDPE film

Specimen: 200um LDPE film
Exposure: Q-U-V accelerated weathering tester, Lamp UVB-313
Cycle Time: 4Hrs. UV at 60°C / 4Hrs. condensation at 50°C
Additive: Antioxidant 0.05% Chinox1076

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure time to 50% retained elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>600 hrs</td>
</tr>
<tr>
<td>0.2% Chisorb944</td>
<td>2800 hrs</td>
</tr>
</tbody>
</table>
Light stability of PP plaques

Specimen: 2 mm thickness injection moulded plaques  
Filler: 0.2% Ca-stearate  
Antioxidants: 0.05% Chinox1010 + 0.05% Chinox168  
Weather-o-meter: Xenon arc weather-o-meter

<table>
<thead>
<tr>
<th>Stabilization</th>
<th>Time to chalking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>700 hours</td>
</tr>
<tr>
<td>0.2% Chisorb944</td>
<td>2100 hours</td>
</tr>
<tr>
<td>0.2% Chisorb519</td>
<td>2450 hours</td>
</tr>
</tbody>
</table>
Fig. The yellowing effect of QUV exposure on epoxy with different pretreatment
After each 200 hrs Exposure
Formulation: Epoxy (anhydride hardener) + 1% UV Absorber (or without),
Exposure: QUV 313, Temp: 50°C
* Outdoor test for 2 months has similar performance

<table>
<thead>
<tr>
<th>Test result</th>
<th>Blank</th>
<th>TP-10</th>
<th>EPL</th>
<th>Benzotriazole UVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat resist</td>
<td>F</td>
<td>O</td>
<td>F</td>
<td>X</td>
</tr>
<tr>
<td>UV resist</td>
<td>X</td>
<td>F</td>
<td>O</td>
<td>X</td>
</tr>
</tbody>
</table>

O: Good, F: Fair, X: Yellowing
New tendency and possible application

• UVA:
  Polymerizable UVA,
  1. For high UVA concentration coating to protect the subject beneath of coating like solar film.
  2. Long term durability, such like automobile paint without migration

Chisorb 5103 for PU, polyester system system
Chisorb 5687 for acrylic, rubber system
Principles of antioxidants
Antioxidants

- Primary antioxidants:
  Chinox 7, 35, S35, 1076, 1010, 1024, 1098, 1330, 3114---

\[
\begin{align*}
\text{ROO}^* + \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{OH}
\end{array} & \rightarrow \text{ROOH} + \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{O}^*
\end{array} \\
\text{ROO}^* & \rightarrow \begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \\
\text{O}^*
\end{array} + \begin{array}{c}
\text{O}^* \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{OOR}
\end{array}
\end{align*}
\]
• BHT
**Chinox 35**

Liquid version of anti-oxidant, designed for polyol application

![Chemical structure of Chinox 35]
• **Secondary antioxidant:**

  Phosphite

  Chinox 168, 618, 626, DP, TP-10...

  \[
  \text{P(OR)}_3 + \text{ROOH} \rightarrow \text{OP(OR)}_3 + \text{ROH}
  \]

• **Thioester**

  Chinox DL

  \[
  \text{S-CH}_2\text{CH}_2\text{COOC}_{12}\text{H}_{25} + \text{CH}_2\text{CH}_2\text{COOC}_{12}\text{H}_{25} \rightarrow \text{OS-CH}_2\text{CH}_2\text{S} + \text{ROH}
  \]
• Metal deactivator:
  Chinox 1024
## Stabilization of LDPE

Additives: 0.05% Chinox1010  
0.05% Ca-St

<table>
<thead>
<tr>
<th>Stabilization</th>
<th>Yellowness Index after 5 times extrusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>28</td>
</tr>
<tr>
<td>0.05% Chinox 168</td>
<td>25</td>
</tr>
<tr>
<td>0.05% P-EPQ</td>
<td>19</td>
</tr>
<tr>
<td>0.05% Chinox626</td>
<td>12</td>
</tr>
</tbody>
</table>
**Phosphate antioxidant for ABS**

**Chinox DP**

<table>
<thead>
<tr>
<th>ABS compounding stage</th>
<th>Chinox 618</th>
<th>Chinox DP</th>
<th>Yellow index (initial)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosage</td>
<td>1000 PPM</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>1000 PPM</td>
<td>350 PPM</td>
<td>9</td>
</tr>
</tbody>
</table>
Reactable Antioxidant

Chinox 528

Advantage:
- Act as a polyol, reactable to carboxylic, isocynate group, used in polyester, urethane system as build in AO without migration

Benefit:
- Direct food contact possible
- Long term lasting performance
- Water borne PU system
Test result in PVC application

<table>
<thead>
<tr>
<th>TEST ITEM</th>
<th>CHINOX 602L</th>
<th>Irganox 245DW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow index</td>
<td>-25.14</td>
<td>-17.99</td>
</tr>
<tr>
<td>Whiteness</td>
<td>63.75</td>
<td>54.22</td>
</tr>
<tr>
<td>b* Value</td>
<td>-8.77</td>
<td>-5.97</td>
</tr>
<tr>
<td>Heat stability (min.)</td>
<td>24</td>
<td>20</td>
</tr>
</tbody>
</table>

Dosage: 200 ppm as 100% solid in PVC latex
All the value is initial color figure of PVC latex after compounding
Performance of Chinox1024

Specimen: LDPE communications wire insulation
Base antioxidant: 0.07% Chinox1076
Failure criterion: crack appears

<table>
<thead>
<tr>
<th>Stabilization</th>
<th>Days oven aging at 110°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>control</td>
<td>6 days</td>
</tr>
<tr>
<td>0.1% Chisorb 1300</td>
<td>153 days</td>
</tr>
<tr>
<td>0.1% Chinox 1024</td>
<td>116 days</td>
</tr>
</tbody>
</table>
New development for PC application

Chinox P-500

Benefit:
- Polymer type acrylic resin, with small dosage could improve degradation problem of PC, polyester, which cause dramatically viscosity dropping

<table>
<thead>
<tr>
<th>Molecular weight, Mn</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1% Chinox P-500</td>
<td>52000</td>
<td>53500</td>
<td>51000</td>
<td>48500</td>
<td>46000</td>
</tr>
<tr>
<td>Without</td>
<td>52500</td>
<td>51000</td>
<td>48000</td>
<td>42000</td>
<td>38000</td>
</tr>
</tbody>
</table>
Applications of plastic additives
PVC application 1

**UVA**
- Flexible PVC: Chisorb 336, BP-12,320
- Rigid PVC: 5411, 327, P

**Antioxidant**
- Chinox 8850

**Heat stabilizer**
- DBM 83
- SBM50 (FDA approval)
PVC application 2

Polymerization stage:

- Suspension or emulsion polymerization, PVC maker will dose antioxidant as chain controller as well as antioxidant.

- DBC designed Chinox 602L as an emulsified water borne anti-oxidant for this application. Its performance have been approved in ABS, Rubber Latex, and PVC application.
PE/ PP application

**General application**: Chinox 1010, 1076, 168, Chisorb 5411, 770, 622, 944

**Agriculture film**: Chisorb 944, 622
- Chisorb 519 for anti-pesticide and acid rain

**Film, Fiber**: Chinox 3114, 1330

**Crosslinkable PE**: Chinox 3114, 1330

**Bumper**: Chisorb 622, 944, 5411, 770

**Cable**: Chinox 1024
Polyamide (Nylon)

- **AO**: Chisorb 1098, 168, 1010
- **UVA**: Chisorb 234, 328, 5431
- **HALS**: 622, 944
- **Anti-NOX**: Chisorb 1300/1500
ABS, PC/ABS, PS

- **AO:** Chinox 8850, 1076, 1010, 7, AO-5400 (polymerization stage), DP, 168, P500, Chinox 602L
- **UVA:** P, 5411
- **HALS:** 770
Polyol application

- BHT is the most common applied in polyol synthesis, which is remain in polyol, and down stream product like PU or UP. As BHT is very easy quench to a quinone, which always cause yellowing or pinking.

- Chinox 35 could solve this problem

- Chinox TP-10H, TP-10, TP-80 is designed to replace TPP with high temperature resist and color stability
PU application 2

Polyether polyol: good hydrolysis, poor weatherability, cheap

Chisorb SUV and 5103 are designed to be used in polyether polyol PUD to improve weatherability.

These products could be easily emulsified to PUD formulation, it is recommended to dose in formulation or synthesis stage.
PU application 3

- **Solvent base PU**: Chisorb 971 covers whole range UV absorption with oxidation protection.
- **Other recommendation**: Chisorb P or 328, with 292, 770 or 622 for coating, resin.
- **TPU**: Chisorb B2661
PU application 4

- **PU foam**:

  Chisorb B2650, SUV both are blend of UV absorber, AO and HALS, have full range covering from UVA to UVB, as well as protection from oxidation. The excess dose of Chinox TP-10 has improving heat resistance.
PU application 5

- **Spandex**:  
  UVA: Chisorb 5103, 326, 234  
  HALS: Chisorb 622  
  Anti-gas fading: Chisorb 1300, 1500

- **Reactive type AO**: Chisorb 528, with 2-OH function remained, play as an antioxidant and polyol could be polymerizable in back borne without migration.
Polyester

- **UVA**: 327, 326, 5103
- **AO**: 1010, 3114
- **Optical brightener**: OB-1
- **Anti-hydrolysis agent**: Chinox P-500
PC application

- UVA: Chisorb 5103, 5411, 325, 234
- AO: Chisorb P-500, 1010, 3114, 1330, 168