Newly developed high performance light stabilizer for greenhouse films

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Agenda

Introduction

- Agricultural PolyOlefin (PO) film market information
- Trend of the Greenhouse film

Newly developed light stabilizer

- Identification of light stabilizer
- Characteristics of newly developed light stabilizer

Advanced light stabilizer technology in Greenhouse film application

- Optimization of sulfur fumigation condition
- Weatherability under severe sulfur fumigation condition
- Weatherability under medium sulfur fumigation condition

Conclusion
Introduction
### Types of Agricultural film

<table>
<thead>
<tr>
<th>Applications</th>
<th>Usage</th>
<th>Requirement</th>
<th>Period [year]</th>
<th>Percentage [%]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Greenhouse</td>
<td>• External covering</td>
<td>• Long term weatherability</td>
<td>3 &lt;</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Transparency</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Heat retention, etc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mulch</td>
<td>• Ground covering</td>
<td>• Mid term weatherability</td>
<td>1~3</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>• Keeping ground temp.</td>
<td>• Color is Black, Silver, Green, etc</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Weed suppression</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silage</td>
<td>• Wrapping preservasion of grass</td>
<td>• Disposable</td>
<td>&lt; 1</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Adhesion during storage</td>
<td></td>
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</tbody>
</table>

* *Agricultural Films Market by Applications & Polymers – Global Trends & Forecasts to 2017*

Long term weatherability has been required for greenhouse application, so the suitable light stabilizer system has to be used.
Demand of PO compounds for greenhouse has been continuously increasing.

*Agricultural Films Market by Applications & Polymers – Global Trends & Forecasts to 2017
The greenhouse films used for long term are exposed to sunlight, so high weatherability is most important. HALS is essential to give long-term weatherability for agricultural film.

**However**

- Pesticide, Sulfur etc… are used for preventing damage to crops from disease and harmful insects. Especially sulfur fumigation is increasing, $2,000 \Rightarrow 3\sim4,000$ ppm in agricultural film
- On the other hand, HALS is inactivated by sulfur and pesticide due to acid-base reaction.
- Low basicity HALS should be necessary for long-term use of greenhouse.
Newly developed light stabilizer
Identification of light stabilizer

**LS-2: 50% Active Component LDPE MB**
- Main component: LS-1 (ADK STAB LA-81)
- Pellet Form

**LS-1 (ADK STAB LA-81)**

**LS-3**
- NO-Alkyl type HALS (commercially available)

**Conventional LS**
- NO-Alkyl type HALS

**Formulae:**
- LS-1: \[\text{C}_{11}\text{H}_{23}\text{O}-\text{N}-\text{O}-\text{N}-\text{OC}_{11}\text{H}_{23}\]
- LS-3: \[\text{NO-Alkyl type HALS} \]
- Conventional LS: \[\text{(ADK STAB LA-94G)}\]
Characteristics of LS-1

Features
- Low basicity
- Low polarity (good compatibility with polyolefins)

Basicity of LS-1 and other HALS

<table>
<thead>
<tr>
<th></th>
<th>LS-1</th>
<th>LS-3</th>
<th>Conventional LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>pKb</td>
<td>11.6</td>
<td>11.4</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Solubility of HALS

<table>
<thead>
<tr>
<th>HALS</th>
<th>Heptane</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS-1</td>
<td>&gt;50</td>
<td>0.1</td>
</tr>
<tr>
<td>LS-3</td>
<td>1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>conventional LS</td>
<td>4.2</td>
<td>0.1</td>
</tr>
</tbody>
</table>

*(g/100g-solvent)*

LS-1 is expected to have an excellent compatibility with polyolefin

*pKb* using pH meter in MeOH
Advanced light stabilizer technology in Greenhouse film application
Formulation

- LLDPE (MFR=2.0) : 100
- Phenolic AO-1 (0.05%) / Phosphite P-1 (0.10%) / Ca-St (0.05%)
- Light stabilizer (1.0 or 2.0%(LS-2))

Processing condition of blown film

- Single screw extrusion \( \varphi 20 \text{mm} \ L/D=25 \)
- Temperature : 190°C
- Ring die
diameter : 25mm, slit width : 0.8 mm
- Film thickness : 40~50 \( \mu \text{m} \)
- Fold width : 80~90 mm
- Winding speed : 4.5~5.0 m/min

Evaluation condition

Sulfur fumigation condition
- Condition A (Severe)
- Condition B (Medium)

Accelerated weathering test
ISO 4892-2 (Xenon-Weather-O-Meter)
- Radiation : 60 W/m²
- WL region : 300-400 nm
- BPT : BST65 °C with water spray
Initial color after processing

Photograph of film after processing

w/o LS  LS-1  LS-2  LS-3  Conventional LS

LS-2 has no negative influence on the initial color of film
LS-2 showed same weatherability as other LS in case of no sulfur fumigation
Optimization of sulfur fumigation condition

Sulfur fumigation treatment

PO film was exposed to sulfur fumed by heating of sulfur on the hot plate in a box.

PO film was put under weathering test.

Sulfur fumigation condition

- Amount of sulfur: 5.0 g
- Heat condition: 160 °C, 4 h
- Sulfur fumigation cycle: Once every 120h exposure

4,000 ppm Sulfur at 3,000h
Machine for tensile test

SHIMADZU AG-Xplus
Speed: 500mm/min
Weatherability ~ Tensile strength ~

With severe sulfur fumigation

LS-2 showed the best weatherability among other LS from tensile strength point of view under severe sulfur fumigation condition
Weatherability ~Elongation retention~

With severe sulfur fumigation

LS-2 showed the best weatherability among other LS from tensile elongation point of view under severe sulfur fumigation condition
Summary-1

Sulfur fumigation condition...

Following sulfur fumigation condition can achieve 4,000ppm sulfur content at 3,000 hours exposure... severe condition

- Amount of sulfur: 5.0 g
- Heat condition: 160 degree C, 4 hours
- Sulfur fumigation cycle: Every 120 hours exposure

Advanced Light Stabilizer, LS-2, could provide...

- Better initial color stability
- No issue on weatherability with no sulfur condition
- The best weatherability under severe sulfur condition
**Medium sulfur fumigation condition**

**Severe Sulfur fumigation conditions**
- Amount of sulfur: 5.0 g
- Heat condition: 160 °C, 4 h
- Sulfur fumigation cycle: Once per **120h** exposure

**Medium Sulfur fumigation conditions**
- Amount of sulfur: 5.0 g
- Heat condition: 160 °C, 4 h
- Sulfur fumigation cycle: Once per **360h** exposure

Graph showing exposure time vs. sulfur concentration, with dashed lines indicating sulfur concentration at 3,000h.
Weatherability ~Tensile strength~

With medium sulfur fumigation

LS-2 showed the best weatherability among other LS from tensile strength point of view under medium sulfur fumigation condition as well.
LS-2 showed same weatherability as LS-1 and LS-3 from tensile elongation point of view under medium sulfur fumigation condition.
Summary-2

Sulfur fumigation condition…

Following sulfur fumigation condition can achieve 2,000ppm sulfur content at 3,000 hours exposure… medium condition

- Amount of sulfur: 5.0 g
- Heat condition: 160 degree C, 4 hours
- Sulfur fumigation cycle: Every 360 hours exposure

Advanced Light Stabilizer, LS-2, could provide…

- The best weatherability under medium sulfur condition as well. However, the performance of LS-1 and LS-3 should also be acceptable.
Conclusion
Conventional LS

<table>
<thead>
<tr>
<th>Sulfur fumigation level</th>
<th>LS-2</th>
<th>LS-1, LS-2 and LS-3</th>
<th>Conventional LS</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;3000 ppm</td>
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<td></td>
<td></td>
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<tr>
<td>1500~3000 ppm</td>
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<td></td>
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<tr>
<td>&lt;1500 ppm</td>
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</table>

Conclusion

Positioning of Light Stabilizer

LS-2 is the most suitable light stabilizer under high sulfur fumigation condition.
Thank you for your attention!

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