Stabilization of Agricultural Films: Basics and New Development

M. Guo, D. Horsey,
Ciba Specialty Chemicals Corporation
Tarrytown, New York

Abstract: Plasticulture wouldn’t exist without plastics. The use of plastics, especially polyolefins, would be limited without stabilizers. Ultraviolet radiation is the primary cause for agricultural film (ag-film) degradation. Various UV stabilizers can interrupt the degradation process and extend the service life of ag-films. These UV stabilizers can be classified into three categories: UV absorbers, nickel quenchers and hindered amine light stabilizers (HALS). UV absorbers are not very effective in thin films. Nickel quenchers provide poor thermal stability and sound environmental alarms. HALS are the state of the art UV stabilizers, but in ag-films, they can interact with certain pesticide derivatives. With nickel quenchers being phase out of the market, developing pesticide resistant HALS becomes a top priority for additives suppliers. The enhanced HALS systems, i.e. Tinuvin 111, Tinuvin 492 and Tinuvin 494, are based on the existing chemistry and offer performance improvement. CGL 116, a new NOR-HALS, offers excellent chemical resistance and high UV stabilization efficiency. This powerful stabilizer will make it possible to make thinner and longer lasting ag-films.

Keywords: stabilization, degradation, agricultural film, new

Introduction

Ag-films are essential for protected cultivation. Polyethylene films are widely used as mulch, greenhouse covering, row covers, high tunnels, silage wraps, etc... Extended exposure to UV radiation, heat and agro-chemicals reduces the useful life of ag-films. Various stabilizers have been used to protect the films against UV degradation, all have their own limitations. The market has been demanding a UV stabilizer with high efficiency and improved pesticide resistance.

Ag-film Degradation and Stabilization

Ultraviolet radiation is the major cause for polyethylene film degradation. Temperature extremes and their duration can also weaken the film. This thermal degradation can especially become a problem where the film makes contact with greenhouse structure. Air pollutants and chemicals used for pest and plant disease control can also cause premature failures [1,2].

Photo-degradation starts with chromophores present in the polyethylene. These chromophores, such as catalyst residues, carbonyl groups and hydroperoxide groups, absorb UV light and move to higher energy levels (excited states, R*). The excited states are reversible, but can lead to the generation of free radicals (R•). The free radicals initiate a chain reaction, quickly reacting with oxygen to form peroxide radicals (ROO•), which in turn react with polymer (R-H) to generate polymer centered radicals (P•) and hydroperoxides (ROOH). The hydroperoxides can be further decomposed into alkoxy (RO•) and hydroxy radicals (HO•), which can again react with polymer and cause further degradation. As a result, film will lose physical properties. The photo-degradation process is illustrated in Figure 1. [3, 4]
The photo-degradation process ultimately destroys the physical properties of ag-films and must be stopped. A number of chemical approaches can interrupt the process.

- **UV absorbers** - absorb UV radiation, interrupt step 1.
- **Nickel quenchers** - deactivate the excited states of chromophores, interrupt step 2.
- ** Hindered amine stabilizers** - scavenge free radicals ($R^\cdot$, $ROO^\cdot$), interrupt step 3 and 4.

UV absorbers are subject to and limited by Lambert-Beer’s law, $A = e b c$, where absorbance $A$ is a function of film thickness $b$. In ag-films, UV absorbers are unable to fully absorb the UV radiation until it has penetrated through part of the surface layers where degradation begins [3].

Nickel quenchers are not limited by the film thickness, but provide poor thermal stability. Heat from the Sun intensifies where the film contacts the greenhouse frames. This heat stress causes nickel quencher stabilized films to break down faster. In addition, nickel quenchers are coming under more and more scrutiny because of environmental concerns [1,4,5].

Hindered amine light stabilizers (HALS) scavenge free radicals without being consumed. They provide both UV and thermal stability to ag-films. However, conventional HALS can be deactivated by acidic derivatives of some agro-chemicals, such as sulfur- and halogen-containing compounds. The exact mechanism of interaction is yet to be determined [4,5,6]. One explanation is that the acid “neutralizes” the basic piperidine nitrogen in the HALS by forming the corresponding salts and partially inhibits its radical scavenging mechanism. It should be noted that nickel quenchers, although more resistant to some chemicals than HALS, are not completely immune to pesticide attacks.

**New Development**

With nickel quenchers being phased out of the market, additives suppliers have to develop more pesticide resistant HALS. There are basically three ways to reduce pesticide interaction.

- To make HALS more sterically hindered. Tertiary hindered amine (NR-type, e.g. Chimassorb 119) are generally less interacting than secondary HALS (NH-type, e.g. Chimassorb 944).
- To lower the basicity of HALS. Less basic HALS will interact less with acidic species.
- To use coadditives. Acid neutralizers can mitigate the pesticide effect.

The desired product should have two features: high UV stabilization efficiency and low pesticide interaction. The conventional HALS tend to have a trade-off between the two features. For example, Tinuvin 622 and HALS-1 have low basicity (pKa ~ 6) but are not as effective light stabilizers as Chimassorb 944. A few new products have been developed to offer both features.

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1 Hostavin® N30
Tinuvin 111 is a synergistic blend of two less interacting tertiary HALS, Tinuvin 622 and Chimassorb 119. Tinuvin 622 contributes the less interacting feature, while Chimassorb 119 offers higher UV stabilization efficiency.

Tinuvin 492 and Tinuvin 494 are enhanced HALS systems based on Chimassorb 119, a less interacting tertiary HALS, and coadditives that neutralize the acidic pesticide derivatives.

CGL 116 is a new generation stabilizer based on alkoxy amine (NOR) chemistry. NOR HALS have less tendency to interact with the acidic pesticide derivatives because of their very low basicity, for example, CGL 116 has pKa of 4.2. Equally important, NOR HALS are very efficient, because they are already in the proper oxidation state to directly enter the HALS stabilization cycle. CGL 116 is a solid, high molecular weight NOR HALS with good polyolefin compatibility. Simulated field tests show that CGL 116 offers outstanding performance in ag-films.

Simulated Field Tests

The best way to assess the effectiveness of a stabilizer is to test the ag-film in the field under real conditions. Exposure in an ideal “clean” environment is meaningless. Acid treatment does not correlate well with the field results [1,6]. Two simulated field tests were designed to evaluate the new HALS products in mulch and greenhouse films.

1. Mulch Test

1 mil LDPE/LLDPE film was used. The film was first treated with methyl bromide, a commonly used soil fumigant, for three days, then strapped on a soil box for outdoor exposure. Elongation was measured as an indication of loss of physical properties.

The test results are shown in Figure 2. Tinuvin 111 and CGL 116 outperformed the conventional Chimassorb 944 and HALS-1. The high performance of CGL 116 is better demonstrated in the following greenhouse study, where the pesticide treatment is more severe.
2. Greenhouse Test

LDPE blown film was tested on a trial greenhouse. The experimental conditions were carefully chosen to differentiate the various parameters responsible for film failures. Permethrin, a chlorine-containing insecticide, was sprayed through a pipe once a month. Metam-sodium, a sulfur-containing soil disinfectant, was applied once every six months. The greenhouse frames were made of galvanized iron and pine wood. Films on “windows”, i.e., without any contact with the frames, were directly exposed to the pesticides sprayed through the pipe two feet below. Films in contact with the support frames had less pesticide exposure than those on “windows”, but experienced more thermal and mechanical stresses. Film samples were taken from window and frames area for physical property testing. Two studies were carried out, one focuses on Tinuvin 492, the other on CGL 116.

Figure 3 demonstrates that Tinuvin 492 outperformed the traditional HALS + UV absorber systems. Compared to nickel quencher, Tinuvin 492 performed better in films on the greenhouse frames, and provided good protection for the films under pesticide attack. Overall, Tinuvin 492 provided a better balanced protection for films.

Figure 3  HALS Performance in 6-mil Greenhouse Film

CGL 116 provides outstanding protection for the films (Figure 4). With severe pesticide exposure (i.e. on windows), CGL 116 was as effective as the benchmark nickel quencher Ni-1, and far better than the conventional HALS, for example, 0.4% CGL 116 outperformed 0.8% Chimassorb 119, the best performer of all conventional HALS in the test. While Ni-1 provides poor thermal stability, CGL 116 does not have such limitations. For films exposed on the greenhouse frames, Ni-1 stabilized films failed dramatically after 21 months, but CGL 116 stabilized films retained 50% elongation after 31 months. The on-the-greenhouse-frame data was incomplete for the conventional HALS, because the films became brittle on the windows and could not be fixed on the greenhouse frames.
Figure 4  CGL 116 Performance in 6-mil Greenhouse Film

In reality, the greenhouse film is one integral piece. If the film breaks down, no matter where, the film fails its function. Because of their different characteristics, nickel-quencher stabilized films tend to break down faster on the frames, vice versa for HALS. In this test, all conventional stabilizers failed after 22 months, while CGL 116 lasted up to 29 months. The overall performance of various formulations is summarized in Table 1.

<table>
<thead>
<tr>
<th>UV Stabilizers</th>
<th>Months to Film Failure</th>
<th>Failure Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4% Ni-1 + 0.2% BZP-1</td>
<td>21</td>
<td>Frames</td>
</tr>
<tr>
<td>0.4% Chimassorb 944</td>
<td>20</td>
<td>Window</td>
</tr>
<tr>
<td>0.4% Chimassorb 119</td>
<td>21</td>
<td>Window</td>
</tr>
<tr>
<td>0.8% Chimassorb 119</td>
<td>22</td>
<td>Window</td>
</tr>
<tr>
<td>0.4% CGL 116</td>
<td>29</td>
<td>Window</td>
</tr>
</tbody>
</table>

Encouraged by the test results from the trial greenhouse, a real greenhouse testing was performed in Spain. The results clearly demonstrates the high efficiency and pesticide resistance of CGL 116 (Figure 5).
Conclusions

Stabilizing agricultural films presents a challenge to additives suppliers. None of the conventional stabilizers can provide a balanced protection for ag-films. With nickel quenchers being gradually phased out of the market, a new stabilizer is needed. Tinuvin 111 and Tinuvin 492, 494 already fulfill the actual requirements. Both are based on the existing chemistry and offer performance improvement. CGL 116, with excellent chemical resistance and superior stabilization efficiency, will represent the next generation of ag-film stabilizers.

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Literature Cited