

**ENHANCED WEATHERABILITY
OF EXTERIOR PVC BUILDING PRODUCTS**

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ABSTRACT

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Poly(Vinyl) Chloride (PVC) is used extensively as a material for the growing building products market. Color preferences of consumers, for markets such as vinyl siding have forced the industry to seriously reconsider the use of PVC especially for the medium to dark color palettes, where the performance is critical. Organotin mercaptides have always been the stabilizers of choice in the US market due to their inherent outstanding heat stabilization properties. On the other hand, this technology is also known to be a compromise between processability and weathering characteristics. In a market that drives for excellence, all additives have to be optimized to meet the final performance requirement. Organotin carboxylates and specifically maleates have long been known for excellent weathering but have not been used extensively in the industry due to less than optimum intrinsic heat stabilization efficiency and in some cases, troublesome lachrymatory properties. A new generation of organotin maleates has been successfully developed to address both issues. This paper will describe the improved lachrymatory behavior of the new technology compared to standard organotin maleates and also will show its outstanding weathering performance in PVC capstock compared to conventional organotin mercaptide during natural aging.

ENHANCED WEATHERABILITY OF EXTERIOR PVC BUILDING PRODUCTS

1. Introduction

The exterior PVC building products market has seen a dramatic increase in the last couple of years, much in line with the growth of the economy and housing starts. Industries such as vinyl siding, profile, fencing and decking have experienced dramatic growth in the past 5 years.⁽¹⁾⁽²⁾

Traditional rigid PVC white and pastel construction products have been supplemented with a whole host of new and innovative value added and consumer oriented additions such as wood filled PVC, foamed PVC and a wider variety of colors geared toward consumer preference and color trends. While a decade ago, the consumer could purchase vinyl siding or window profile in white or pastel shades, the new millennium has evolved to feature vinyl building products in mid tones and darker tones (especially as accent trim) as well as with special looks such as variegated and stainable wood filled vinyl.

In order to sustain acceptable growth in some of the more mature markets, such as vinyl siding and window profiles, innovation and improvement needs to continue. The outer limits of the products' capabilities need to be expanded. For example, PVC siding has not historically been seen in the market in any large volumes in darker colors, however, there has been an increase in the market preference by the consumer for darker and darker colors. What was once a white dominated market is now dominated by a whole color palette ranging from white to dark reds and browns. Further proliferation of this

trend will require advanced technologies; ones that improve the weatherability of such colors as well as solve the heat distortion issues associated with heat build up in darker colors. Traditionally, US exterior PVC building products have been stabilized with organotin mercaptans, known for their extreme efficiency as heat stabilizers and their good weatherability in lighter colors containing sufficient UV stabilization via high levels of titanium dioxide. Further development of more challenging color palettes will require improved technology. The new technology will either consist of non-PVC highly weatherable (but more costly) alternative polymer capstocks over traditional PVC substrates, or improved formulation (additives and/or resin) and processing for enhanced weatherability of existing PVC capstocks.

Organotin maleate stabilizers have been used for decades as an improved stabilizer technology imparting better PVC weatherability. Their growth has been limited by their more difficult processability and their tendency to be lacrymators. This paper will explore the development of a new type of maleate technology designed to improve upon these two limiting tendencies.

2. Lachrymatory study of organotin maleate

Organotin maleates have long been known to have lachrymatory properties, which made their use somewhat limited in PVC. Under standard PVC processing conditions, lachrymatory by-products such as maleic anhydride or low molecular weight maleate esters can be formed by decomposition of the thermal stabilizer. These by-products have

the potential to irritate workers via the vent of the extruder or from the fumes at the extruder die. Based on a NIOSH method (Method 3512), a test was designed to monitor vapors coming off of PVC during processing and model the behavior for a commercial extruder. The total amount of vapors identified, mainly as maleic anhydride, was quantified as a function of time and correlated to the optimized chemistry. To demonstrate the low lachrymatory behavior of this novel chemistry, it was compared to two other commercial solid organotin maleate stabilizers. Indeed, solid organotin maleates tend to have a lower lachrymatory effect than the liquid ones, which have lower molecular weight and higher vapor pressure.

2.1. Experiment:

Two experiments were run to compare the lachrymatory behavior of a new maleate (Maleate A) with dibutyltin maleate and dibutyltin bis stearyl maleate.

1. Neat stabilizers were heated at 200°C for 30 min under static conditions
2. A standard rigid PVC siding capstock formulation containing a much higher level of stabilizer (5 phr) in order to maximize the lachrymatory effect was processed in a Brabender under typical conditions using 65 grams of compound, 190°C and 75 rpm.

For both experiments, the vapors were absorbed as a function of time in a known volume of solvent using a volumetric pump.

2.2. Results:

The results expressed in terms of weight sublimed are summarized in **Tables 1** and **2**.

The results clearly indicate the significant reduction of lachrymatory product evolution during the stabilizer degradation. This improved behavior was obtained by the chemical modification of the maleate structure to increase its inherent thermal stability. Thermogravimetric Analysis (TGA) results displayed in **Table 3**, can give an idea of the thermal stability of the neat stabilizer by measuring the mass loss as a function of the temperature during a heat ramp. This table summarizes the temperatures needed to achieve 5% and 10% mass loss. Maleate A shows at least 20 degrees higher in decomposition temperature compared to the other solid maleate stabilizers.

Indeed, these results have been demonstrated in a production environment where a formulation containing Maleate A was subjected to the day-in, day-out rigors of commercial extrusion, including power outages where the formulation was forced to sit in a hot extruder for long periods of time.

3. New Hope for PVC Weathering

Three years of outdoor weathering was completed in three US standard weathering sites representing Northern Industrial (Pennsylvania), hot and humid (South Florida) and hot and dry (Arizona) climate. The study involved 24 different color pigments from medium to dark color range. The various pigments were supplied by Holland Color (**Table 4**) Among all the different colors studied; only a few examples, representative of the entire

data set, will be discussed here. The point will be to demonstrate the improved weathering performance in color systems known for their tendency to “chalk” or lighten.

3.1. Experiment

Two typical formulations were processed by both milling in a two-roll mill and by extrusion. The compounds containing various color pigments were blended independently in a high shear mixer. The formulation used is displayed in **Table 5**.

The Processing conditions for both extrusion and milling are the following:

Extrusion: (Leistritz 27mm twin screw extruder): Screw Oil – 180°C, Barrel Zone 1 – 170°C, Barrel Zone 2 – 180°C, Die Zone 1 – 195°C, Die Zone 2 – 195°C, RPM = 25.

Milling: Roll Temperature - $200 \pm 2^\circ\text{C}$, Charge 275g, Gap Setting – 0.79 mm, Speed – 25 rpm, Friction 1-1.2

Dart Drop Impact was run following ASTM D-4226 method A on 0.040 inch samples.

3.2. Weathering of Milled versus Extruded Samples

It appears more and more critical to design tests that can allow a fast and meaningful screening of potential weatherable candidate formulations. The two-roll mill is an efficient means of preparing samples, since not only it is a fast process but it also requires much less material than the extruder. It is well known and has been long demonstrated that PVC weathering is directly a function of the quality of the processing. For equivalent stabilization, high shear, high temperature processing would decrease color

weatherability of the finish part. For that matter, it could be believed that milled samples could have a significantly different weathering behavior than extruded ones and not be representative of the real world. To simplify the presentation and avoid the confusion of too much data, only delta L values, indicative of known phenomenon such as whitening or chalking, will be discussed. Other data values are available on request, however not deemed as relevant to the discussion. Delta L represents the color lightening intensity in the CIELab system. For this study, all samples were milled and extruded to produce samples for weathering.

The two-roll mill can be used to bring a lot of shear and thus imitate quite well the mixing behavior of an extruder. **Figure 1** shows that within the test conditions, the weathering trends measure with milled samples are very similar to the one observed for the extruded. The samples database shows that this remains true regardless of the color and the weathering site. The data presented in this paper were obtained from the milled samples.

Variations in the weathering performance could also be expected to be seen to some degree between samples extruded on a lab extruder versus samples extruded on a production-sized extruder.

The data presented later in this paper will be based on 36 months weathering of milled samples. Similar data is available for extruded samples.

3.3. New Light on Enhanced PVC Weathering

Figures 2a to 4c are a small subset of the data of the weathering performance of a formulation stabilized with the new maleate stabilizer versus a formulation stabilized with a high tin content commercial weatherable tin mercaptide (existing commercial type capstock formulation).

Weathering on these samples and many more in different colors is continuing up to 5 years.

With regard to the lightening or chalking effect seen typically in these types of colors, the new maleate stabilizer (Maleate A) definitely provides enhanced performance in the toughest locations for this type of failure (Northern Industrial and Southern Humid). Impact testing of the samples over time have shown them to be equivalent in performance.

There have been many reviews over the last thirty years on the subject of PVC photodegradation and a large number of them refer to the enhanced performance of organotin carboxylate compared to organotin mercaptans⁽³⁻⁶⁾. Although Organotin carboxylate/maleate high-performance as weatherable systems for PVC have always been known, they have not been extensively used in the industry due to the poor intrinsic heat stabilization performance⁽⁷⁻⁸⁾. An optimization of the fundamental chemical structure of the organotin maleate has allowed us to completely reconsider this old knowledge and offer a new concept capable of not only being an efficient heat stabilizer but also maintaining PVC integrity during weathering. **Table 6** gives an overview of the comparative impact retention for 0.040-inch samples stabilized with mercaptan and

maleate technologies during weathering. Considering the typical impact specifications for siding of 60 inch.lb, the minimum impact value for 0.040-inch samples is 2.4 inch.lb/mil. The data displayed show that in most weathering conditions; the impact properties of PVC are maintained with either technology. The poor impact retention in Arizona passed 12 months with both technologies is due to the high degree of thermo-oxidation encountered in this hot and dry climate that leads to intense backbone chain scission.

4. The Economics of a Pure PVC Capstock solution

While there are other capstock technologies that typically are noted for their good weatherability such as fluoropolymers and acrylics, they usually come attached to a higher price tag than a typical PVC capstock. In many applications, especially in very dark color ranges, they are certainly worth the higher price. The use of a maleate stabilized PVC capstock will give improved weathering performance over standard mercaptide stabilized PVC capstocks with a more reasonable price than most alternate polymer capstocks. Additionally, it will allow for hidden cost savings due to the fact that it will process more closely to a standard PVC capstock than any of the alternatives, with no capital investment required. Many times, alternative polymer capstocks process at significantly different extrusion conditions (temperatures, amps and feed) than standard PVC capstocks, requiring longer times between changeovers which leads to increased scrap and therefore, cost.

5. Conclusion

In order for market growth of rigid PVC building products to continue, innovation and improvements in technology are needed, to allow penetration of these products into areas from which they are presently limited due to technical characteristics. Breakthroughs in technology could allow market expansion into currently limited geographical areas such as the Southwest and could bring a wider color palette offering to the consumer. A new maleate stabilizer for rigid PVC building products has been shown to have significant weatherability advantages over existing, currently utilized PVC stabilizer technology. Additionally it has been shown to have better processing and lachrymation properties than existing maleate stabilizer offerings while being significantly less expensive than alternate capstock polymer approaches. It is hoped that the use of this and other technology developments geared toward improvement of weathering of PVC capstocks will facilitate strong market growth for the rigid PVC building products industry in the years to come.

Acknowledgements

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TABLES

Table 1: Measurement of lachrymatory behavior of neat organotin stabilizer in terms of weight sublimed

Stabilizers used	Weight Sublimed (mg)*
Dibutyltin Maleate	50.6
Dibutyltin Bis Stearyl Maleate	37.4
Maleate A	19.7

* Weight sublimed from 10g of stabilizer at 200°C for 30 min.

Table 2: Measurement of lachrymatory behavior of PVC Capstock Formulations in terms of weight sublimed

Stabilizers used	Weight Sublimed (mg)*
Dibutyltin Maleate	36.1
Dibutyltin Bis Stearyl Maleate	36.5
Maleate A	19.5

- Weight sublimed from 4.2% of stabilizer in the formulation.
- Brabender: 65g/195°C/75 rpm

Table 3: TGA analysis of standard maleate stabilized formulations

Stabilizers used	5% mass loss	10% mass loss
Dibutyltin Maleate	176.2	230.0
Dibutyltin Bis Stearyl Maleate	191.6	225.2
Maleate A	219.6	248.4

TGA conditions: 10°C/min in N₂

Table 4: Holland Color pigments

Color	Reference
White	6970
Light Beige	6961
Light Gray Blue	6964
Gray	6958
Gold	6960
Yellow	6959
Taupe	6957
Green	6963
Dark Beige	6962-01
Dark Gray	6956-01
Dark Gray Blue	6965-01
Brown	6971
Rust	7072-01
Dark Green	7073
Teal	7344
Dark Blue Green	7102
Dark Blue	7071
Dark Brown	7068
Dark Gray II	7070-01

Table 5: Typical PVC Capstock Formulations

Formulation	Standard System	Enhanced System
PVC	100.0	100.0
External Lubricants	1.1	1.05
Internal Lubricants	0.0	0.2
Calcium Stearate	1.2	0.0
Acrylic Lubricant	0.0	0.2
Lubricating Process Aid	0.7	0.7
Impact Modifier	6.0	6.0
Titanium Dioxide	10.0	10.0
UV stabilizer	0.0	0.5
Commercial High tin content Organotin Mercaptan	0.6	-
Maleate A	-	3.0

Table 6: Dart Drop Impact evaluation

Impact*	Initial	6 months	12 months	18 months	24 months
Pennsylvania					
Maleate A	3.2	3.5	3.4	3.0	2.9
Weatherable Mercaptan	3.4	3.7	2.7	2.4	2.8
Florida					
Maleate A	2.9	3.4	3.0	2.4	3.1
Weatherable Mercaptan	3.4	3.1	1.9	2.1	1.4
Arizona					
Maleate A	3.0	3.5	-	1.4	1.5
Weatherable Mercaptan	2.9	3.4	-	0.8	0.4

Impact measured in inch.lb/mil

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Figure 2b: Weathering of milled **light gray blue** samples in South Florida

Figure 2c: Weathering of milled **light gray blue** samples in Arizona

Figure 3a: Weathering of milled **dark gray** samples in Pennsylvania

Figure 3b: Weathering of milled **dark gray** samples in South Florida

Figure 3c: Weathering of milled **dark gray** samples in Arizona

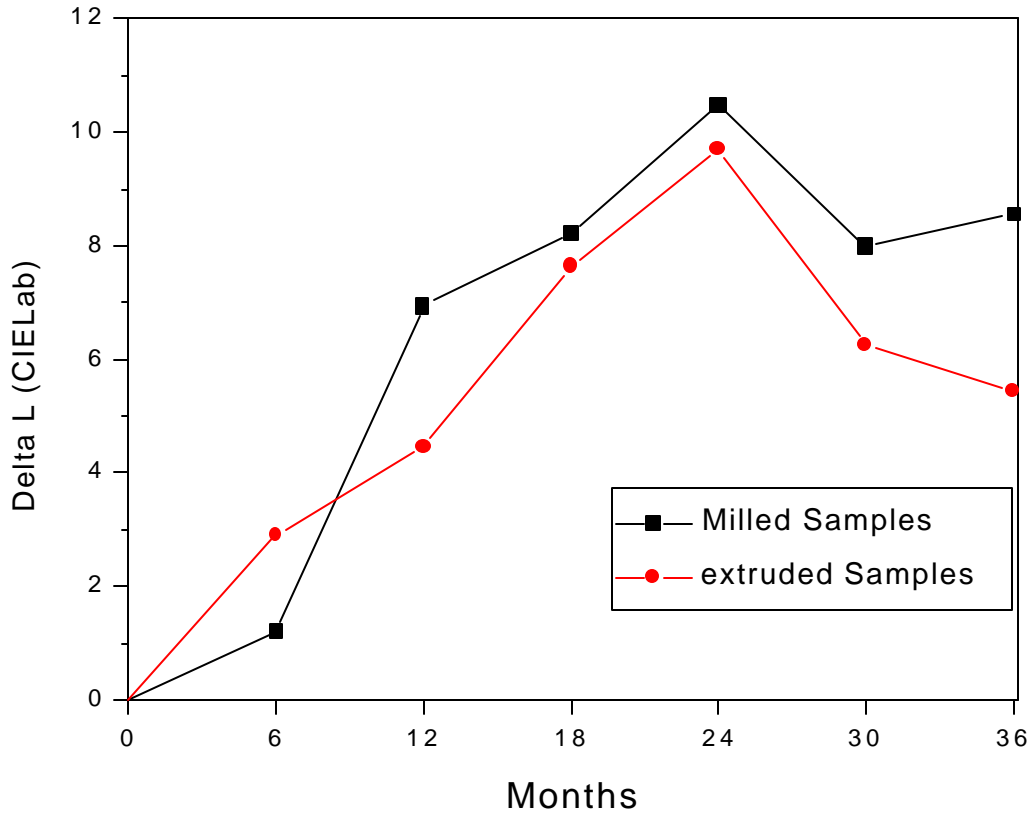
Figure 4a: Weathering of milled **dark beige** samples in Pennsylvania

Figure 4b: Weathering of milled **dark beige** samples in South Florida

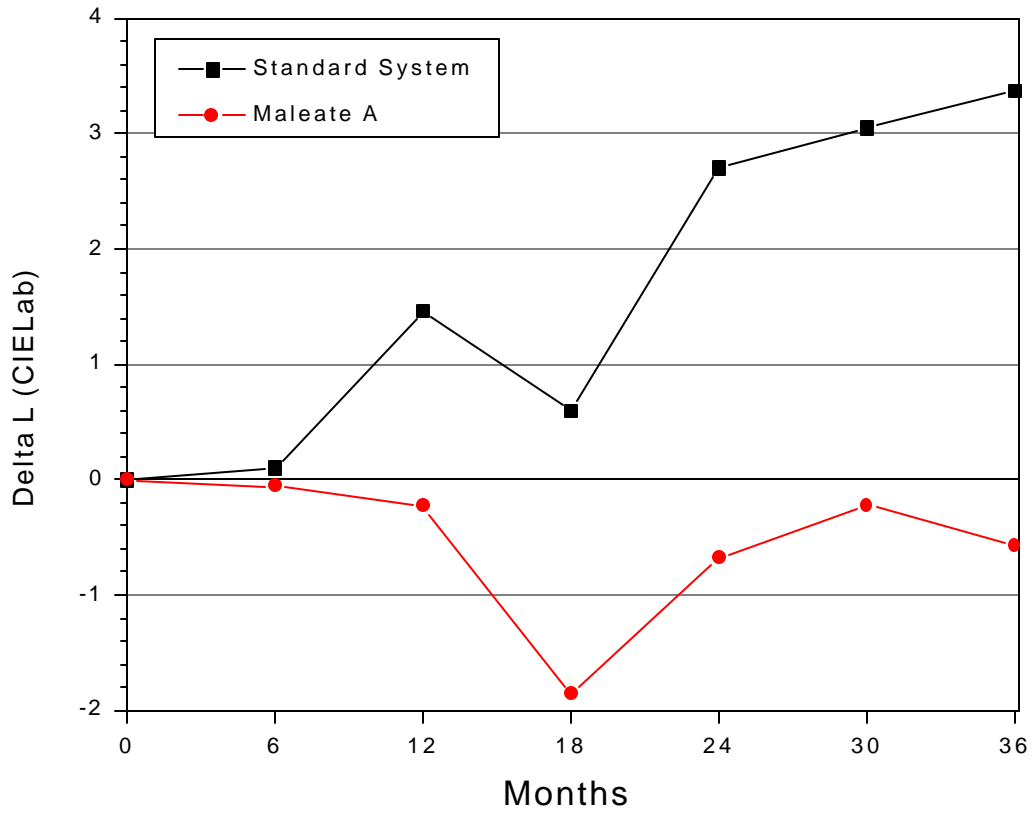
Figure 4c: Weathering of milled **dark beige** samples in Arizona

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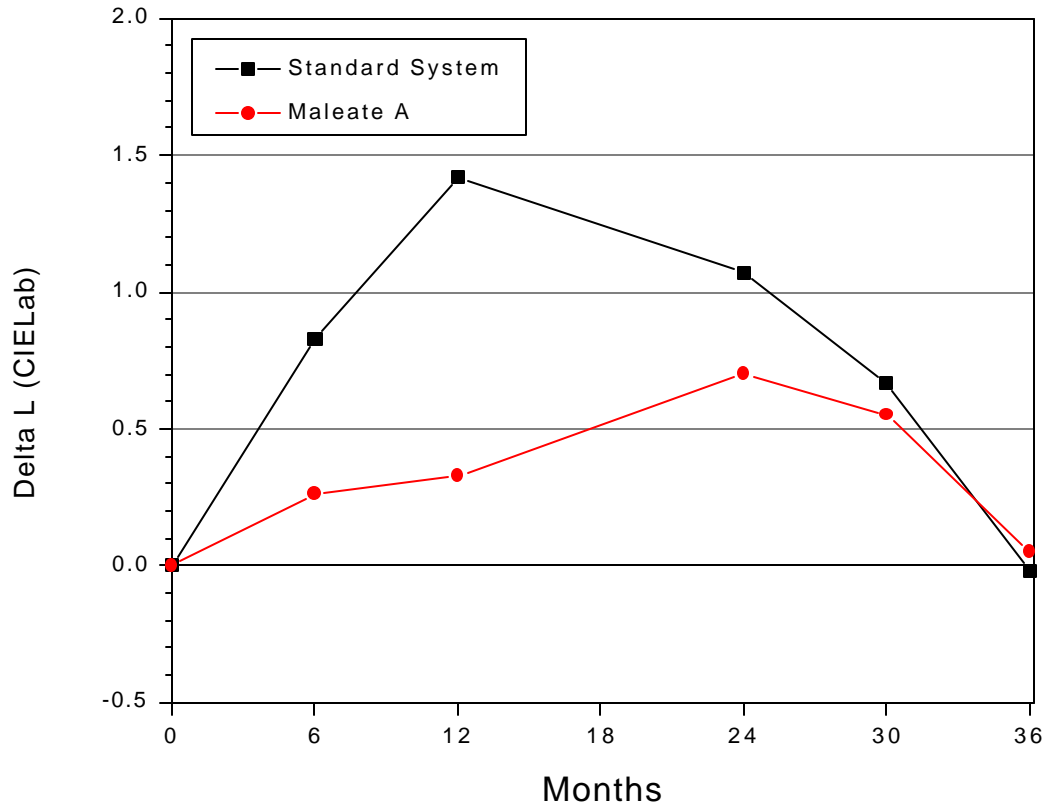
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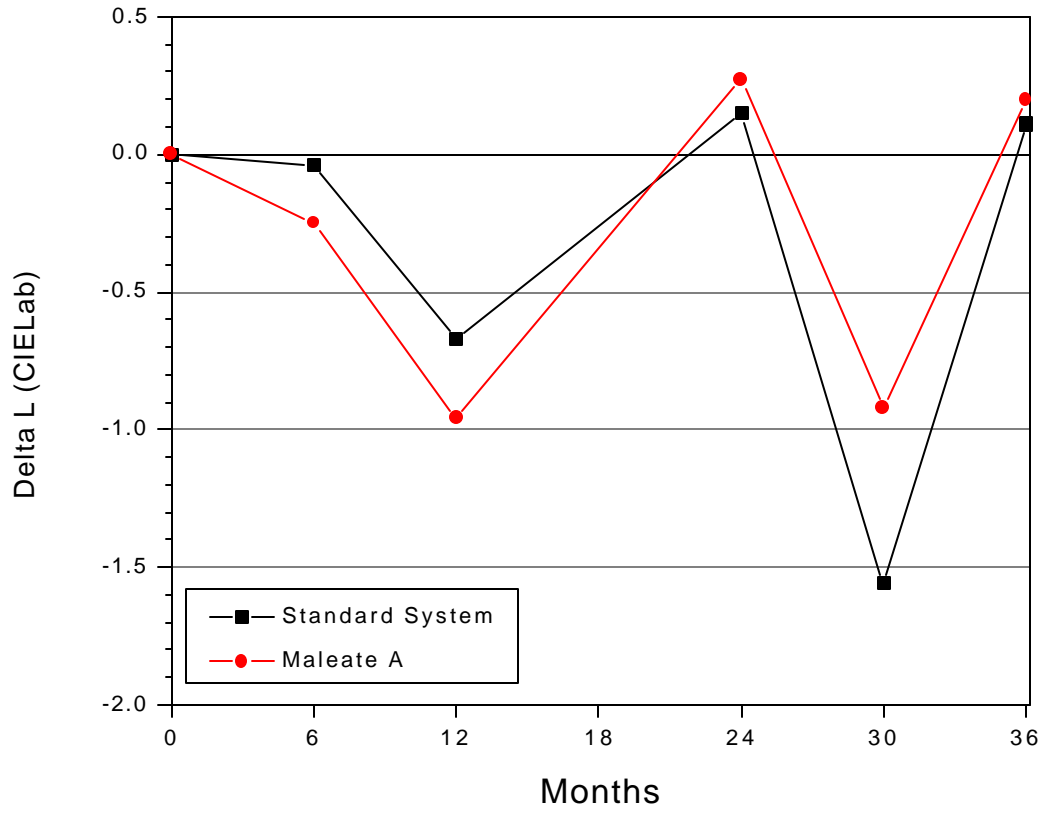
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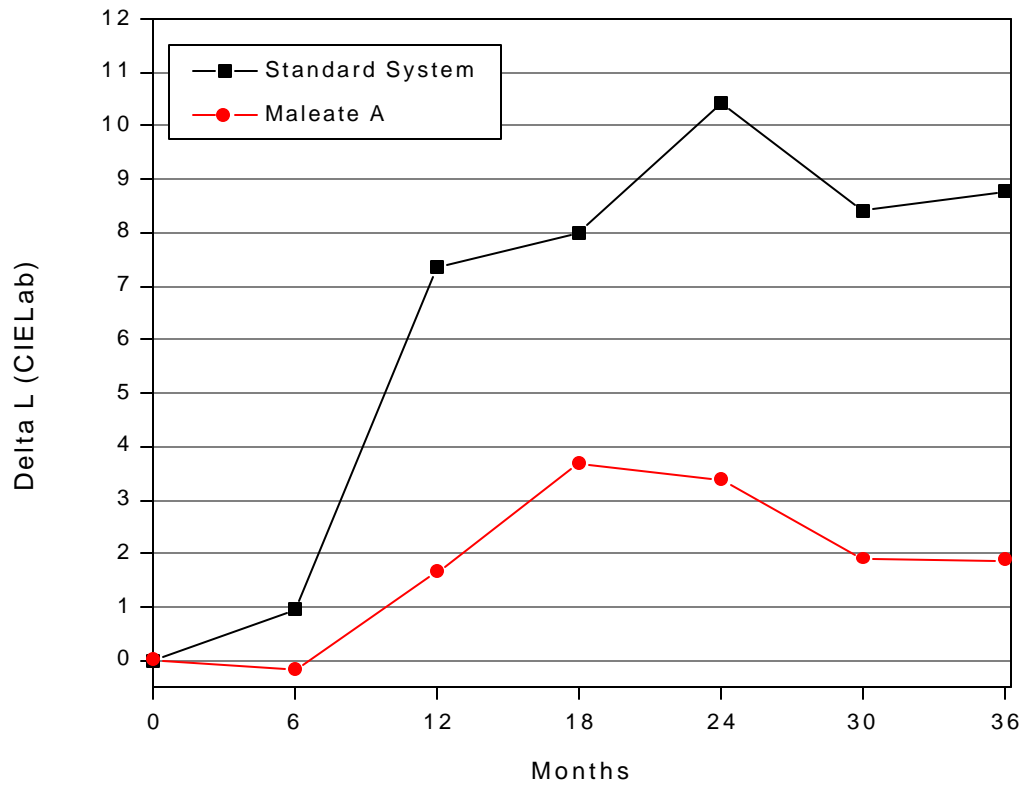
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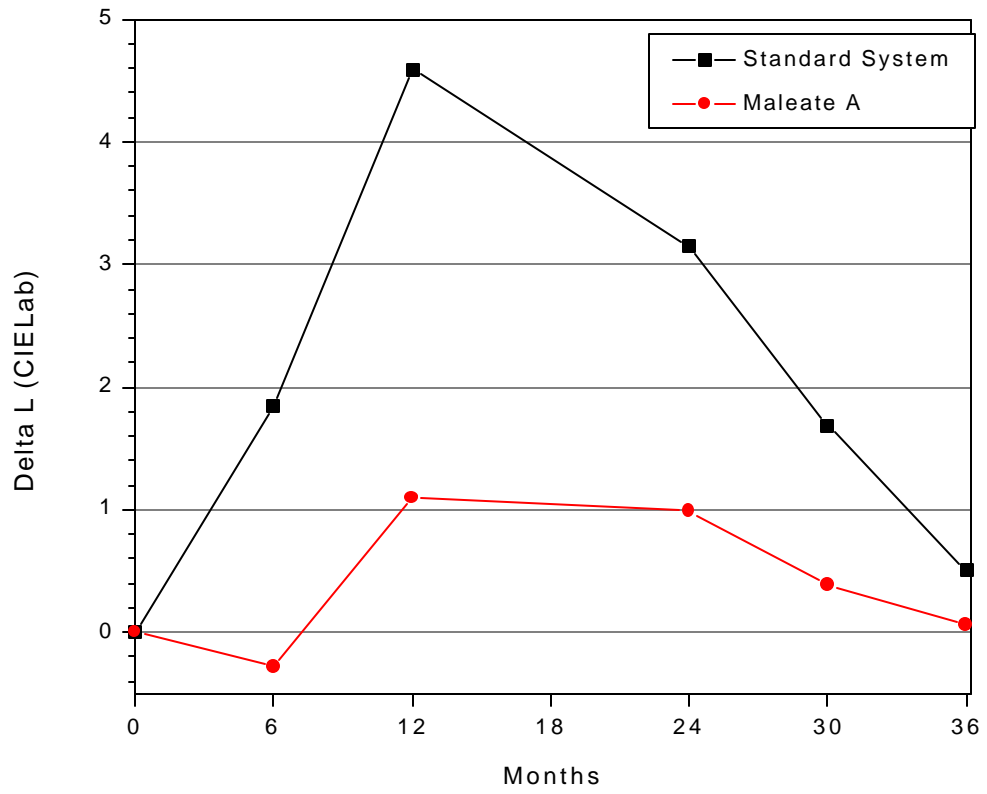
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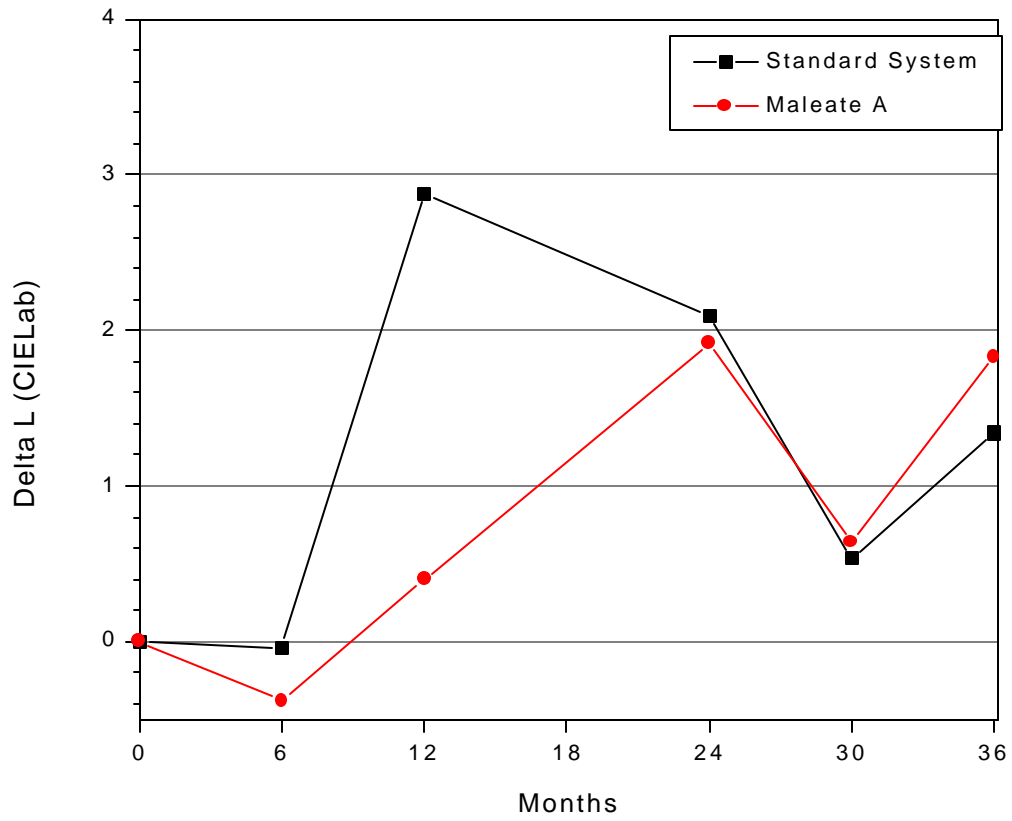
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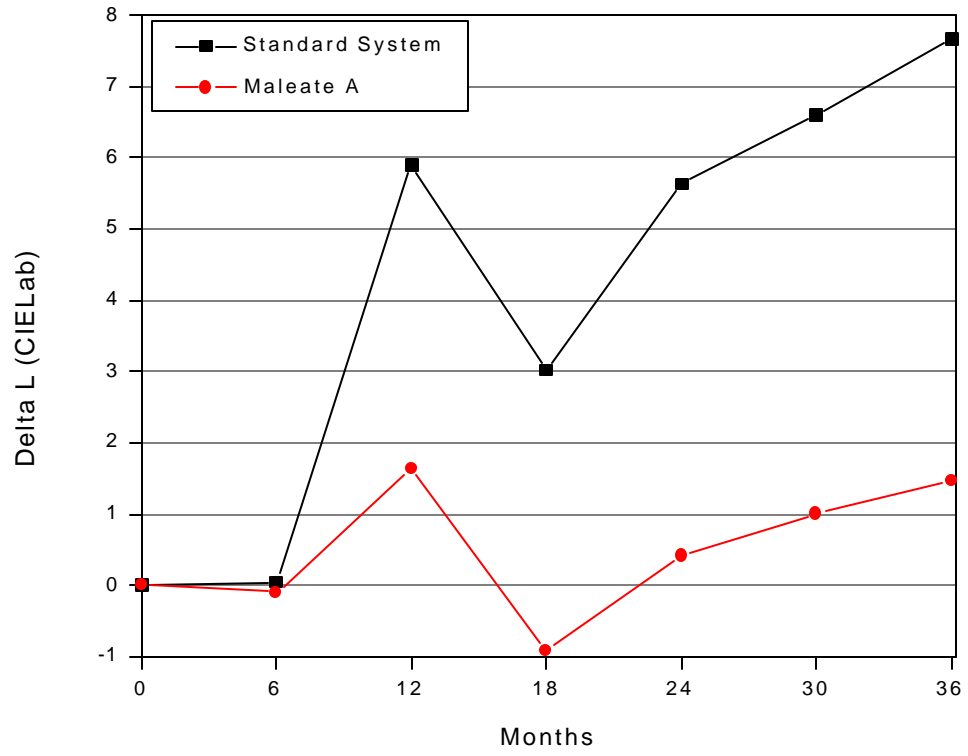
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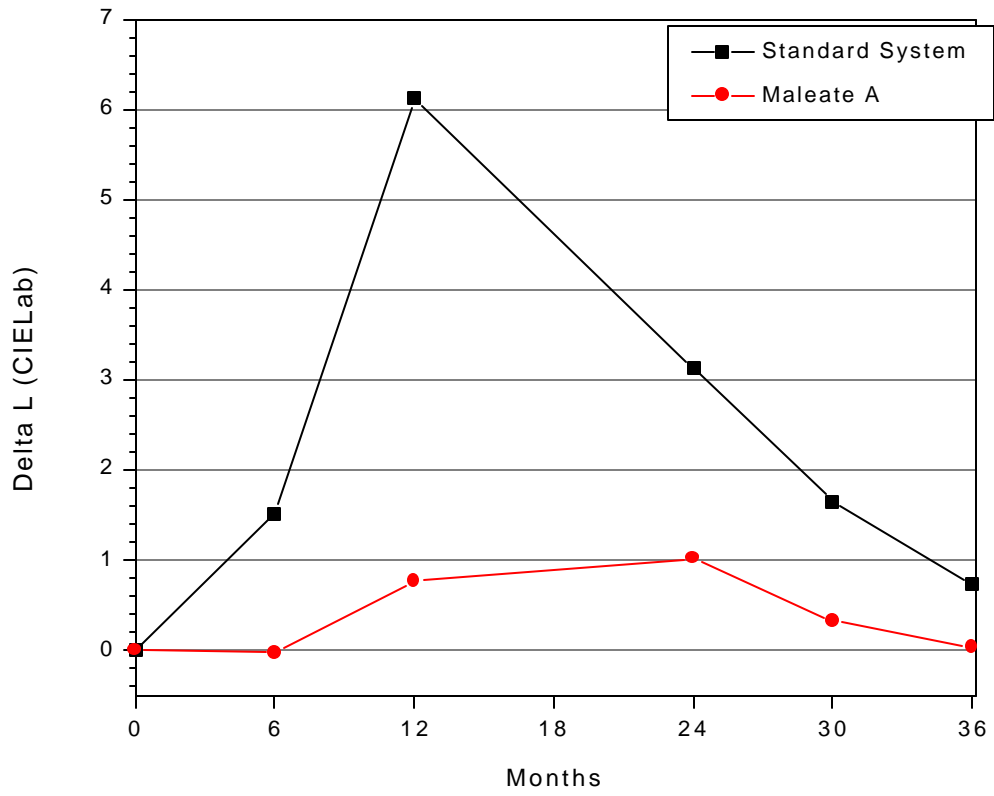
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Girois, Fig.4a



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