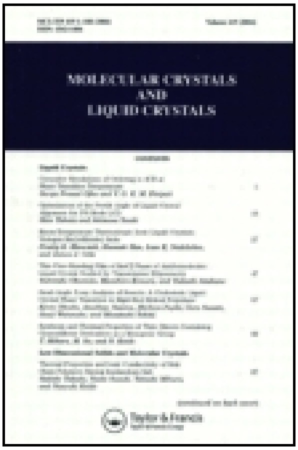

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Photochromic Plastic Stabilization and Matrix Interactions

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There are two primary factors limiting the commercial success of photochromic (PC) plastics, the relatively short lifetime of the finished products and their high cost. We attempted to produce a PC masterbatch with superior stability so that:

- lifetime is significantly increased at equivalent PC dye concentrations when compared to competitors' products.
- dye concentration can be reduced (lower cost) and residual color can also be reduced (performance enhancement) at comparable lifetimes with competitors' products.

In order to achieve superior stabilization, we followed an *Edisonian* (trial and error) and statistical approach. Lifetimes have been extended over twenty times when compared to unstabilized plastics following this approach.

Keywords: Photochromic; photochromism

OVERVIEW

There are two primary factors limiting the commercial success of photochromic (PC) plastics, the relatively short lifetime of the finished products and their high cost. To address these issues, our goal was to create a PC masterbatch with superior stability. Superior stability offers significant advantages in the market:

- lifetime is significantly increased at equivalent PC dye concentrations when compared to competitors' products.
- dye concentration can be reduced (lower cost) and residual color can also be reduced (performance enhancement) at comparable lifetimes with competitors' products.

To achieve superior stabilization, we chose a uncommon approach. While most PC research work is focused on synthesizing more inherently stable PC dyes, we chose practical and "back-end" approaches to solving the problem. The practical approach focused on an *Edisonian* (trial and error) rather than a *theoretical* understanding to controlling the degradation. The back-end approach involved using the known commercially available stabilizers and resins to stabilize the PC dyes. This effort, while quite time consuming and expensive, does yield reliable and meaningful results.

STABILIZERS

Stabilizers are used to slow down the rates of degradation reactions at initiation and propagation, or to increase the rate of termination reactions. There are five commonly available classes of stabilizers, as briefly discussed below [[1]].

1. HALS – Hindered amine light stabilizers, or HALS, are a relatively new class of stabilizers. Their general mechanism for stabilization is free radical scavenging, but also includes energy transfer or peroxide decomposition. They are often highly effective because they regenerate. They offer an additional benefit for PC systems in that they usually do not absorb UV radiation.
2. Antioxidants – Antioxidants work by interfering with free radicals. Their primary method is free radical scavenging and hydrogen donation, and the secondary method is by metal deactivation and peroxide decomposition.
3. Thermal – Thermal stabilizers perform similarly to antioxidants but are usually designed to be most effective at higher temperatures (>100°C).

4. Quenchers – Triplet state quenchers work by transferring the energy from excited chromophores into thermal energy.
5. Ultraviolet – Ultraviolet absorbers work by absorbing ultraviolet radiation and converting it into thermal energy through tautomerism. Special care must be taken with PC plastics so that the range of UV light that is needed for PC excitation is not absorbed by the UV stabilizer. UV absorbers often have limited effectiveness because their performance is a function of Beer's law: they need to be used in high concentrations and require relatively long pathlengths in order to absorb enough UV light to be effective.

STABILIZATION

We began by testing the performance of commercially available resins, HALS, antioxidants, thermal stabilizers, quenchers, and UV absorbers. Our stabilization efforts were broken down into three phases: inherent performance, single stabilizers, and combined optimization.

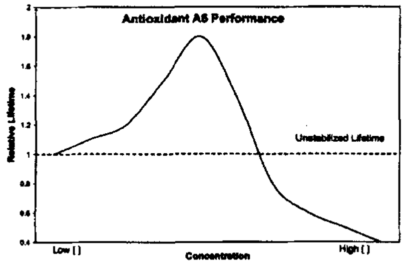
Inherent Performance

The first set of experiments began with selecting the best combination of dyes and resins (without stabilizers) while evaluating five parameters:

Color – the full range of the visible spectrum
Coloration – the least residual color and most intense excited color
Stability – the longest lifetime
Kinetics – no significant change in excitation or fade rates
Cost – the lowest cost of materials for a given level of performance

Single Stabilization

The best inherent performing dyes/resins were then tested with a wide range of individual stabilizers from each of the previously discussed classes. These tests had to be conducted at varying concentrations in order to



observe the changing lifetime effects as shown in the graph above.

The lifetime effects of single stabilizers ranged from 0.03 to 6.1 times the lifetime of the original unstabilized dye in that particular resin. Many of the stabilizers actually hurt the performance of the unstabilized PC plastics.

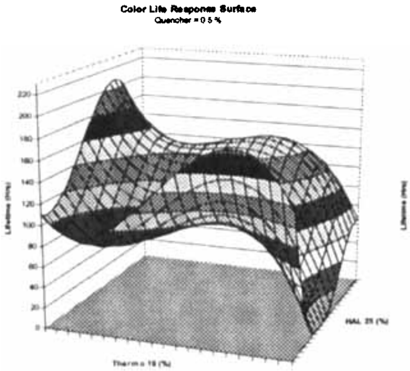
Combined Optimization

The top performing single stabilizers were then combined to optimize the overall stabilization. These multivariate experiments are particularly challenging to conduct efficiently due to the many co-varying concentration-dependent variables involved. Concentrations and combinations of each of the single stabilizers were varied and the resulting stability was measured. This process was repeated as necessary. The tests were further complicated by the following observations:

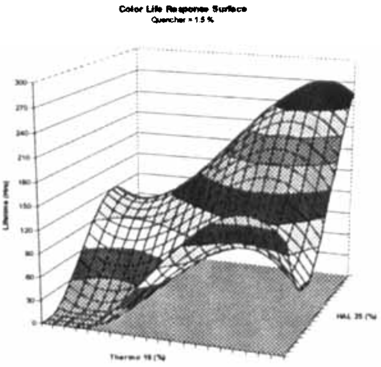
1. Significant unpredictable interactions, both positive and negative, between stabilizers were quite common. For example, the best antioxidant and the best UV absorber significantly under performed the combination of the third best antioxidant and second best UV absorber. The multitude of combinations becomes overwhelming if just the top five individual stabilizers from each class are tested at only three concentrations.
2. Often conflicting results were achieved. The stabilizer that maximized lifetime often also unacceptably increased residual color or induced an undesirable change in color.
3. Even under accelerated degradation conditions, the time required for degradation testing became significant as stabilization performance increased. Second or third generation optimizations took up to 30 days per test.

The effects of the various stabilizer combinations on lifetime were then analyzed using a somewhat complex proprietary statistical model.

The following examples show the very complicated interaction effects that usually occurred during stabilization. The PC dye, UV absorber, and antioxidant concentrations were held constant, while the concentrations of HALS and thermal stabilizers were optimized at different quencher concentrations. As the quencher concentration was varied, the concentrations of HALS and thermal stabilizers required to achieve maximum lifetime also changed as shown below.



Color Life Response Surface
Quencher = 0.5 %



Color Life Response Surface
Quencher = 1.5 %

The results of the combined optimizations led to over a 20 times improvement in lifetime when compared to the unstabilized PC dyes.

MATRIX INTERACTION EFFECTS

There was a range of matrix interaction effects with the PC dyes including stability, kinetics, color, and coloration. Many of these changes can be explained by the differences in resins, primarily through manufacturing differences and morphology properties. There were even significant matrix interactions with the same grade of resin from different manufacturers.

Stability

Unstabilized PC dye 5-3 from PPG lasted 2.5 times longer in our PP than PE. Reversacol aqua green dye lasted more than 3 times longer in PP than PE. Other dyes lasted longer in PE than PP, and some did not even change color in PS, yet worked fine in PE and PP.

Kinetics, Color, and Coloration

Many of the dyes changed color in different resins or exhibited different fade rates. Some dyes even changed color in the same grade of resin from different manufacturers, even though we used the purest materials with the fewest additives available.

For example, Reversacol aqua green showed the following matrix interaction effects.

Matrix Interaction Effects – Kinetics, Color, and Coloration			
Resin	**Residual**	**Excited**	**Fade Rate**
Polyethylene (PE)	Light blue	Turquoise blue	fast
Polypropylene (PP)	Light blue	Intense royal blue	fast
Polystyrene (PS)	Blue	Dark emerald	slow (2x)

Conclusion

The stabilization of PC dyes in plastics is an extremely challenging task. The stabilization is complicated by the multiple interaction effects shown between the dyes, resins, and stabilizers. By using a practical and Edisonian approach, lifetimes in excess of 20 times the unstabilized PC plastics have been achieved.

References

[1] R. Gächter and H. Müller, Ed., *Plastics Additives Handbook*, 4th Edition, Hanser Publishers, Munich, 1993.

[2] J. C. Crano and R. J. Guglielmeiti, Ed., *Organic Photochromic And Thermochromic Compounds*, Volume 2., Kluwer Academic/Plenum Publishers, New York, 1999.