

# **Roles of Colorants, Stabilizers, and Formulated Compounds in Determining the Life Expectancy of an Exterior Composite.**

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## **I. Introduction**

To a large degree, the working life span of an exterior composite is dictated by the ability of the base polymer(s) to resist degradation from heat, ozone, humidity, chemicals, and ultraviolet light. The durability of the composite with respect to these items is dictated by numerous factors, including fillers, additives, chemistry of the base polymer, and also, the colorant which is used. In the event that a working exterior formula needs improvement, innovative means of achieving longevity with strong performance are often required. This is especially true in instances when costs are of critical concern.

There are several ways to approach stabilization of polymers. One of the strongest methods has consisted of analyzing the polymer chemistry, and linking its structures to known mechanisms of degradation. This methodology is well established to practitioners of material science.

In the case of exterior exposure, ultraviolet radiation from the sun is a major contributor to degradative processes. Many colorants possess absorptive and refractive characteristics in regions of the UV spectrum. Changes in the visible spectrum often originate from chemical processes affected by ultraviolet light. Because the objective of colorants in composites is to obtain and maintain a constant color and appearance, these relationships add substantial iterations to the process of formulating durable exterior materials; color science is needed to assure a stable product.

This paper examines relationships between color science, polymers, and stabilizers, and their bearing upon the longevity of composite materials as dictated by humidity and ultraviolet light. In process, several pitfalls are identified, and some rules are constructed for employing color in the science of material stabilization.

## **II. Scope**

Five composite formulations were included in this research: an epoxy, a urethane, and three thermoset unsaturated polyesters. Each compound plays a significant role in identifying colorant based features of exterior degradation. For instance, an obvious reason for including thermoset urethane foams, is that aromatic (e.g. MDI) based urethanes are notoriously vulnerable to ultraviolet radiation. Another, is the value and commonality of properties that this compound shares with many types of thermoset polymers. A third, less obvious reason, is

that urethane foams are a relatively inexpensive way of obtaining high volume composite parts with low density. The aromatic-based urethane was included because it is an excellent vehicle for identifying some of the fundamental mechanisms of UV degradation. As this work demonstrates, these principles have broader application. The source of the urethane's utility is largely a matter of density.

The specific gravity of the urethane foams tested in this study varied from 0.50 to 0.70. Because of blowing agents inherent to the formula, the molded urethane of this work formed a thin, mutable skin across the mold interface which covered an underlying cell structure. Because surface changes, especially erosion, expose the underlying porosity of the urethane composite, it was possible to note when even relatively small amounts of physical degradation had occurred. Because UV degradation often includes surface changes, blown urethanes are helpful for detecting surface erosion hundreds of exposure hours before the event is perceptible in a non-foaming sample. As a result, we obtained clearer identification of mechanistic stability issues which are common throughout a fairly broad range of composite species.

The presence of the epoxy in this study makes it possible to demonstrate the stabilization of yet another type of ultraviolet sensitive polymer. More importantly, it helps to generate data about the degradative principles of varying types of composite materials.

Unsaturated polyesters were essential to this work because of the extensive use of such materials in the thermoset composite industry. Polyesters are also generally less sensitive to physical degradation from ultraviolet light than aromatic urethanes, or two component epoxies. The three unsaturated polyesters included:

- 1) a methacrylate modified, exterior grade polyester, hereafter referred to as "System A";
- 2) a styrenated, interior grade polyester, hereafter referred to as "System B";
- 3) a generic styrene-modified polyester formula, called "System C."

Inclusion of these formulas assisted our efforts to determine what roles were being played by pigmentation in the stabilization of composites. In particular, a comparison of colorant stability in the first two systems illustrates relationships between colorants, stabilizers, system quality, and UV durability that are of paramount importance to designing the best (as well as the most cost effective) system.

Composite failure, as related to this study, can be defined in terms of color change, or of physical degradation, such as through embrittlement and/or loss of surface integrity. These modes of property loss can be attributed to polymer degradation, or to lightfastness failure of the colorant. This paper examines these phenomena, and attempts to draw meaningful conclusions about relationships

that exist between the two distinct modes of failure.

### **III. The Course of Colorant and Polymer Degradation.**

Discoloration of neutral and white colored composites is measurable as a decrease in substrate reflectivity in specific regions of the visible spectrum. This is observed at wavelengths of 370 - 430 nm, and about 650 nm, in the visible region of light. These changes result from chromophore formation upon exposure to ultraviolet light. They occur readily in neutral colored polyester systems as well as white urethanes and epoxies. However, these changes are less visible in black colored systems. Instead, other changes become prominent. Black colored systems were found to undergo loss of gloss (meaning broad, general surface reflectivity), and lose surface integrity as a function of polymeric decomposition. For the purposes of our work, this loss of surface integrity is referred to as erosion. As noted earlier, changes in surface characteristics caused the pore structure underlying the surface of the urethane to become exposed. Erosion, therefore, was found to be the lifespan determining factor in black colored urethanes.

White urethanes however, did not undergo significant erosion in our testing; loss of gloss was observed, but not until after significant and detrimental color change had already caused failure. Color change was found to be the deterministic mechanism of composite failure in light colored urethanes.

In epoxies, a color change was again evident in lighter colors, but less perceptible in blacks. White epoxies yellowed rapidly, and then darkened; under the same conditions of UV exposure, black epoxies discolored only slightly, but lost gloss and chemical resistance over time. This corresponds exactly with the color-based mechanisms observed in our studies of urethanes.

In contrast with epoxies and urethanes, a methacrylated polyester (System A) undergoes only moderate polymeric decomposition in an exterior environment. Light and dark colors in this system typically produced durability in accordance with the quality of the colorant deployed. On the other hand, the styrenated polyester (System B) demonstrated much greater discoloration than a methacrylate based composite. Does this mean that in System B, the rules of urethanes and epoxies apply? Is it possible for a styrenated polyester to provide similar colorfastness to a methacrylated system? Do colorants play intrinsic roles in dictating the durability of a composite polymer? For that matter, is it possible to achieve strong colorfastness in a red epoxy? Can a color durable polyester be formulated of lesser quality colorants and/or other raw materials?

At the time of this writing, just over 1000 hours of weathering data existed on polyester Systems A and B, compared to 2000 hours for all other composite formulas. Under the conditions of our testing, each thousand hours (1250 kJ) corresponds roughly to about nine month's exposure in southern Florida. While

the possibility of future developments in these systems cannot be ruled out, the data produced thus far illustrates several possible answers to these (and other) dilemmas.

#### **IV. Results and Discussion.**

Urethanes containing varying levels of titanium dioxide and carbon black were examined. Two color spaces were proposed, featuring low color value, essentially black tones, and high-color cream moldings featuring titanium dioxide as the sole colorant. Like samples of other composite systems, block moldings were tested in Miami Cycle weathering, using an Atlas 65-WR Weatherometer with xenon arc source radiance. Three grades of carbon black were tested in this study, consisting of: (1) a low-structure carbon used through the coatings and thermoset plastics industries; (2) a high-structure black known commercially for its ability to impart strong UV resistant characteristics; and (3) an ultra-high strength colorant more common to the specialty and high performance products found in both of the above named industries.

The urethane investigation utilized two controls for the evaluation of data. The first, shown in Table 1, contained 4.1% of dispersed colorant, based upon weight percent of system, with no stabilizing additives. The second consisted of 0.68% generic stabilizer, with 3.4% of the unstabilized dispersion. Although dispersion content varied, formulations were adjusted in order to maintain constant concentration of active colorant. As stated earlier loss of surface integrity via chalking and erosion, was found to determine the effective lifespan of black urethane composites. Failure was defined as being the point at which less than 90% of the original surface remained. Color change was observed to be insignificant as degradative contributor beyond the first several hundred hours of exposure, as severe physical failures evolved.

White urethane testing included three distinct grades of titanium dioxide (Table 2). Dry pigment concentration varied between two (2) and three (3) percent of the total formulation. It was found that the grade of pigment utilized did not significantly alter performance, but that changes in concentration may have produced some effect. In this phase of evaluations, facial degradation was (other than chalking) not found to be a significant contributor toward failure. Of far greater interest, was the control of yellowing. This does not imply that titanium dioxide prevents surface degradation, or that carbon black causes it while preventing yellowing. Rather, these trends are representative of the fact that differing color spaces possess unique properties with respect to ultraviolet degradation, as viewed by an observer.

Like the urethane system of this study, the epoxy composite was found to be sensitive to surface and color change. Black and white tone epoxies were evaluated for correlation to the same colorants as used in urethane testing. Also, synergisms observed in urethane experiments were deployed in several red

tones. Some instances of good and bad formulating technique were discovered from these trials.

The filled polyester System "C" was evaluated in red and yellow, against a constant white tint base of eighty percent white colorant and twenty percent yellow as the control. Three yellow colorants of varying exterior durability were proposed. It should be noted that the two exterior grade colorants both exhibited strong colorfastness in this testing; the term "high grade," as applied to the latter refers to its essential inertness with respect to ultraviolet radiation, and in no way detracts from the quality of the first exterior colorant. For the interest of compounders using wear-sensitive processes, each of the yellow experiments was replicated with a zinc sulfide base, for contrasting with the titanium dioxide standard. In this experimentation, yellow samples were controlled for constant color, and incremental adjustments of colorant were necessary to maintain color value when changing pigments; improvements in lightfastness of yellow pigments were associated with decreases in color strength (This is a phenomenon specific to the colorant and color space particular to this research, and should not be interpreted as universal rule). By contrast, a cost-effective, medium quality exterior red was found to be lower in strength than a high performance red colorant. The high grade pigment also provided cleaner color. It is important to note that the red colorants used in the polyester are the same pigments as used in the epoxy composite area of this research.

Polyester Systems "A" and "B" were tested more extensively than System "C". In these two systems, the objective was not simply to compare colorants, but to examine the effects of these colorants between systems of varying durability. Zinc sulfide was compared to titanium dioxide, this time in a white tone, at equal concentration. Black colorants (from urethane and epoxy research) were also included. Red and yellow experiments of System "C" were replicated, but this time with the emphasis on comparing performance of two alternative modifications to a given polymer base. One would expect that under conditions of equal exposure, a methacrylate modified polyester would exhibit higher durability than a styrene modification to the same. Similarly, one would expect a higher grade colorant to produce greater constancy of color than a lesser grade colorant. However, as the following tables illustrate, issues of composite durability can be far more complex.

Table 1. Lifespans of Black Urethanes in Accelerated Weathering

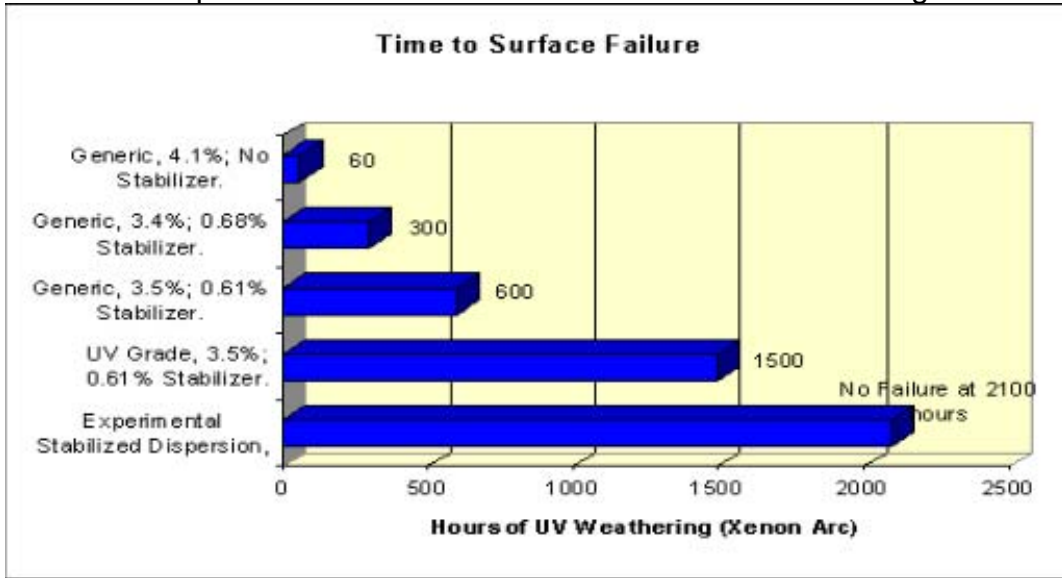
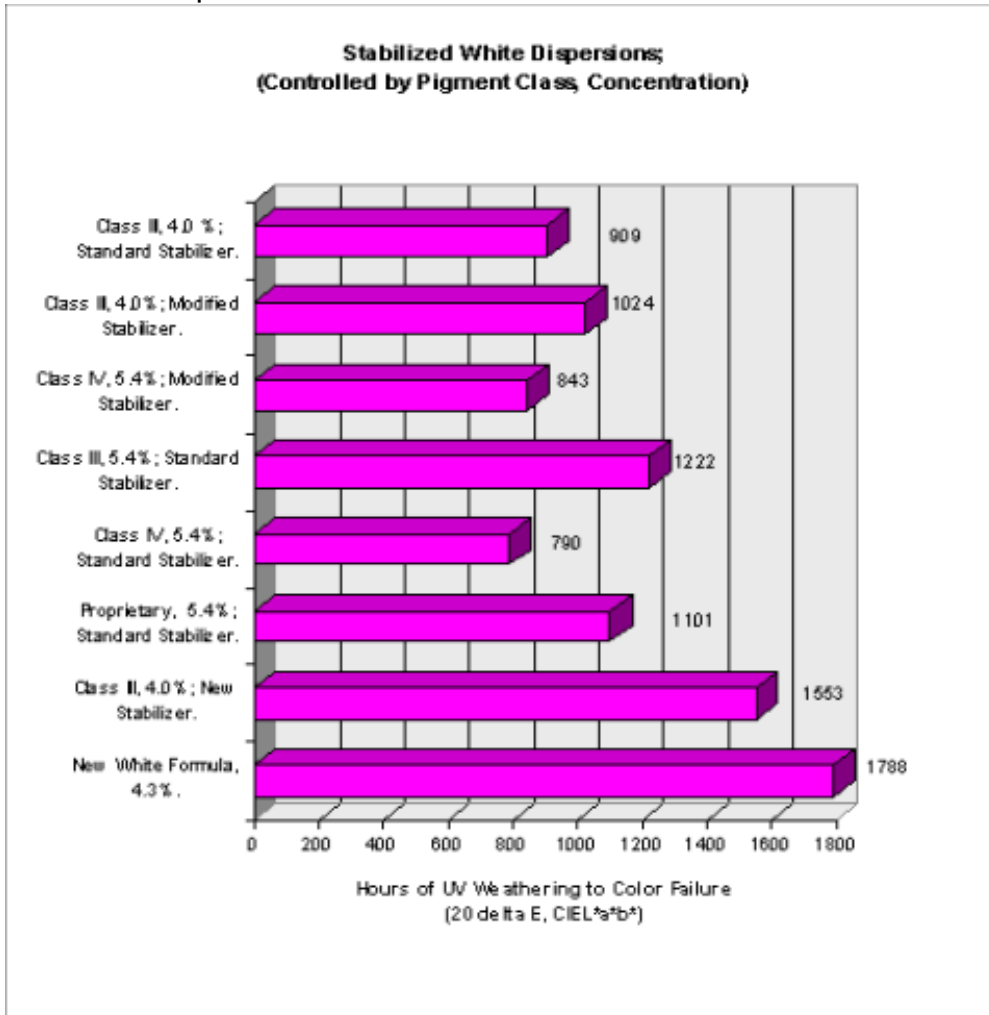


Table 2. Lifespans of Cream-Colored Urethanes in Accelerated Weathering.



In Table 1, loss of facial integrity is observed as pores beneath the surface are exposed. In this black aromatic urethane, polymeric decomposition caused by exposure to UV radiation and humidity leads to erosion of the surface, causing failure. In Table 2, polymeric decomposition leads to yellowing which is measured colorimetrically. The process of yellowing continues until the parts reach a total color difference of about twenty delta E (CIEL\*a\*b\*), at which point chalking and appearance change become dominant.

Table 3. Effects of 100 Hour White Epoxy UV Weathering Test.

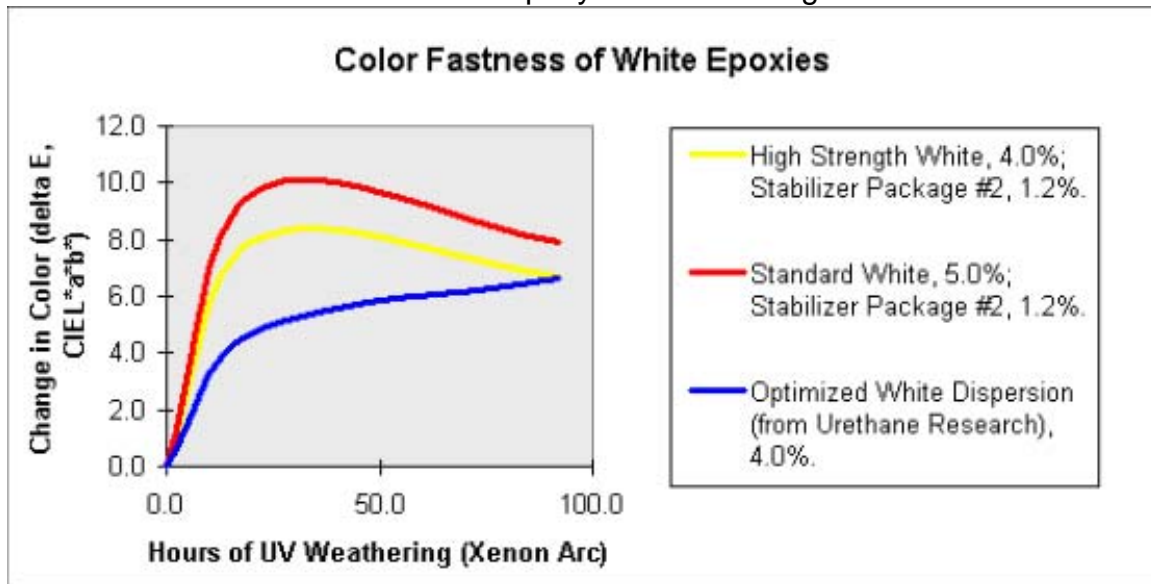
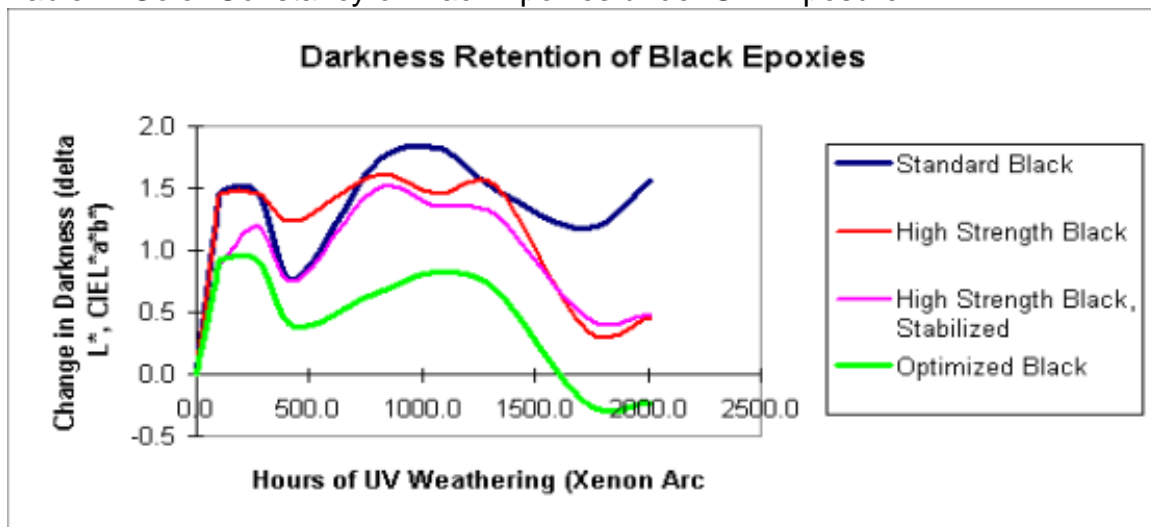


Table 4. Color Constancy of Black Epoxies under UV Exposure.



Tables 3 and 4 demonstrate a pattern similar to that of urethanes, but in white and black epoxies. White epoxies undergo rapid color change (first hundred hours), even when strongly stabilized. Black tones, by contrast, demonstrate color drift that is fractional by comparison, even hundreds of hours into weathering. The potency of the stabilizer/colorant synergism can be measured by the amount of chemical resistance which is exhibited after 2000 hours of exposure. The optimized black dispersion provided 80% surface retention after double-wiping with acetone, as seen in Table 5.

Table 5. Black Epoxies: Retention of Chemical Resistance Properties after 2000 hours Miami Cycle Weathering (Xenon Arc).

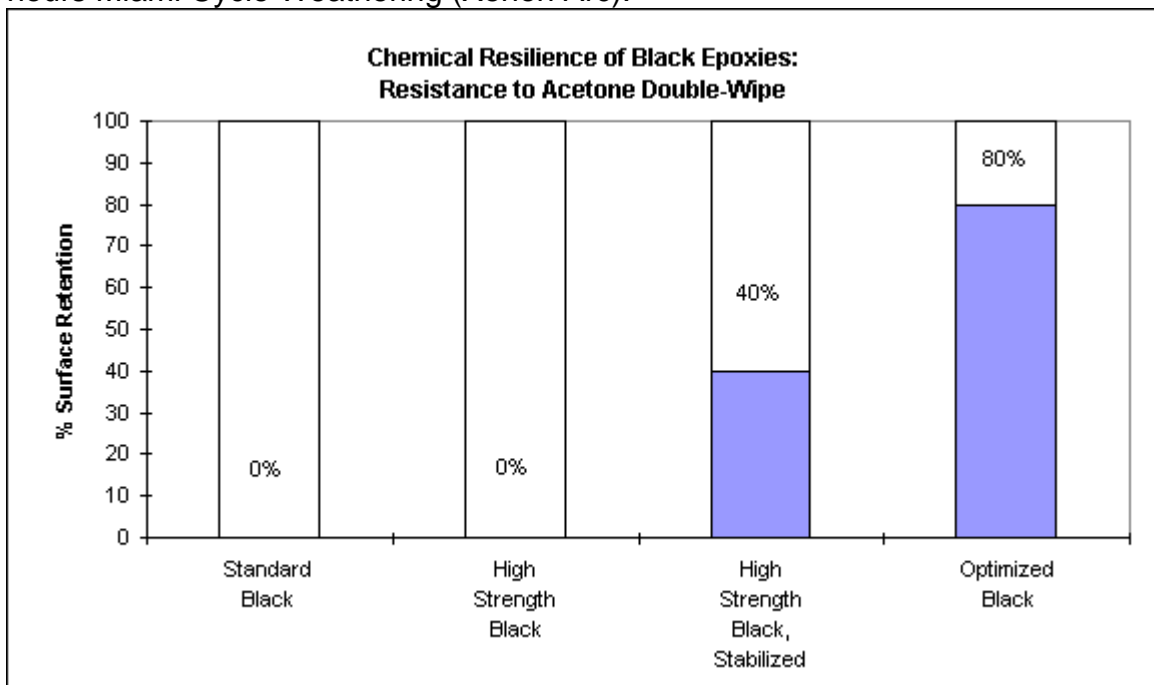
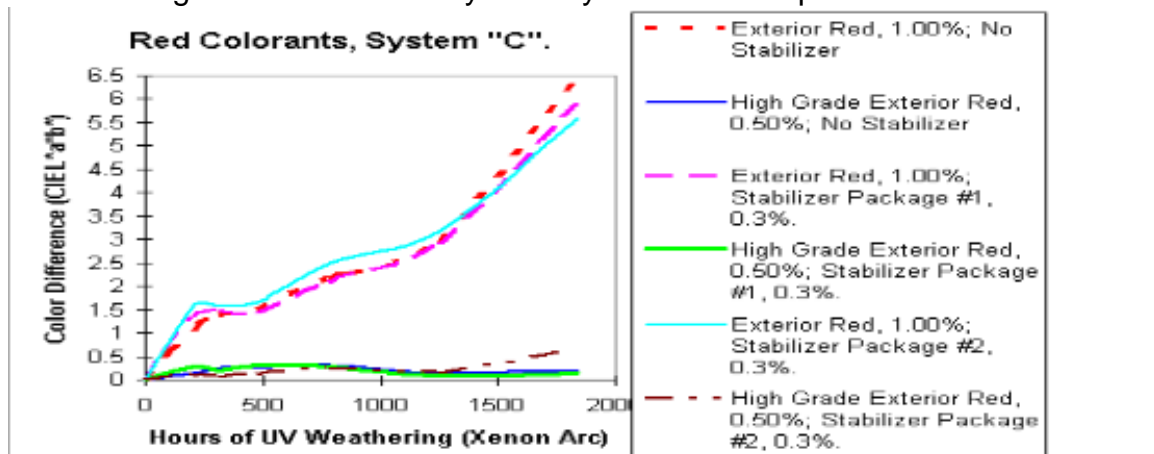


Table 6. Degradation of Red Polyester System "C" Composites.



In Table 6, a classic example of color theory is shown: under conditions of equal weathering, a more durable colorant will provide greater color constancy. Polyester System "C" was selected for its ability to demonstrate color principles. Compare this example with the results of Table 7, where the same colorants are deployed in an epoxy composite.

Table 7. Degradation of Red Unfilled Epoxy Composites

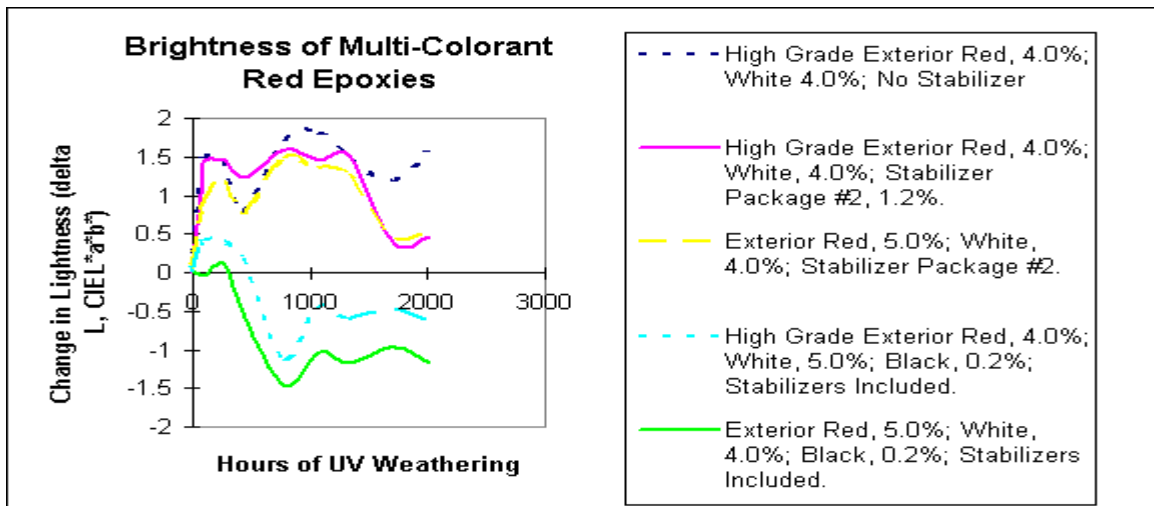
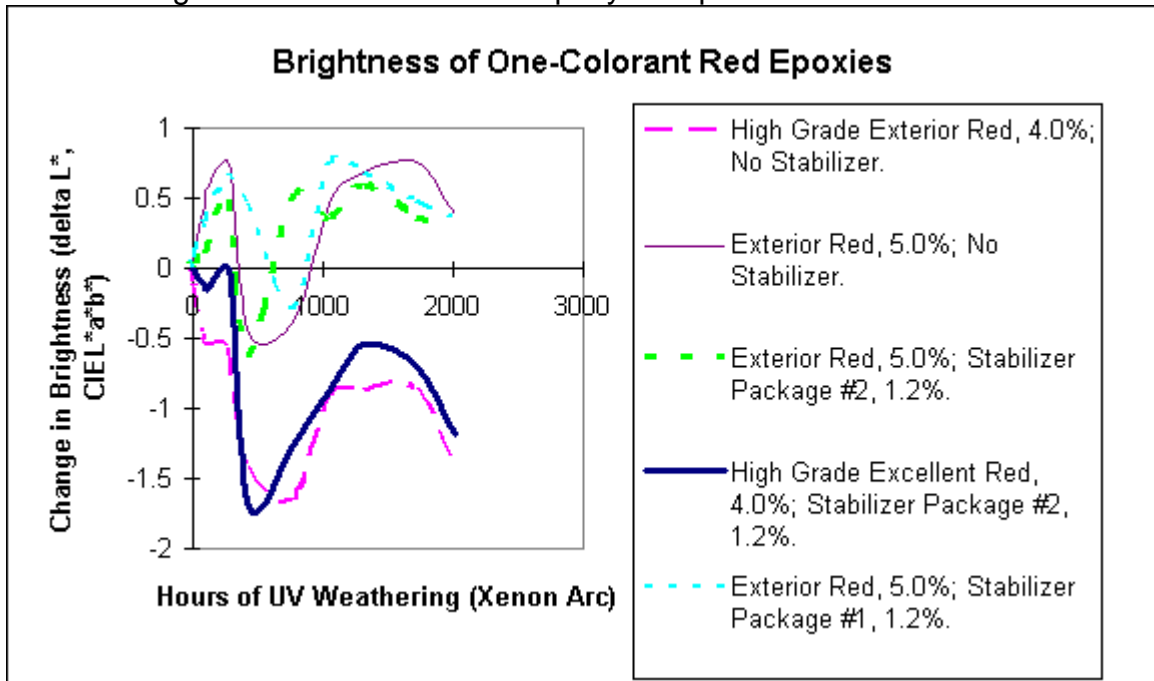
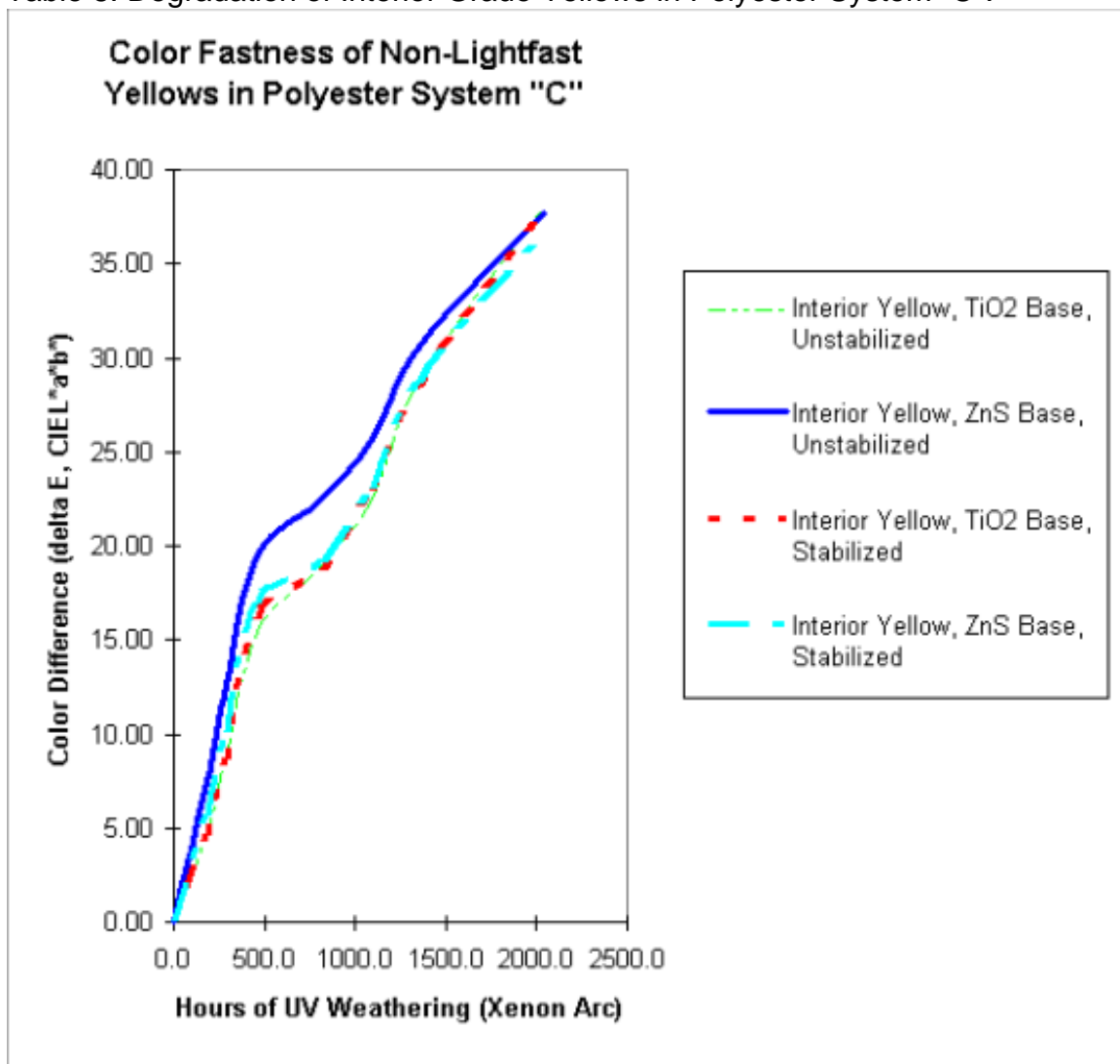


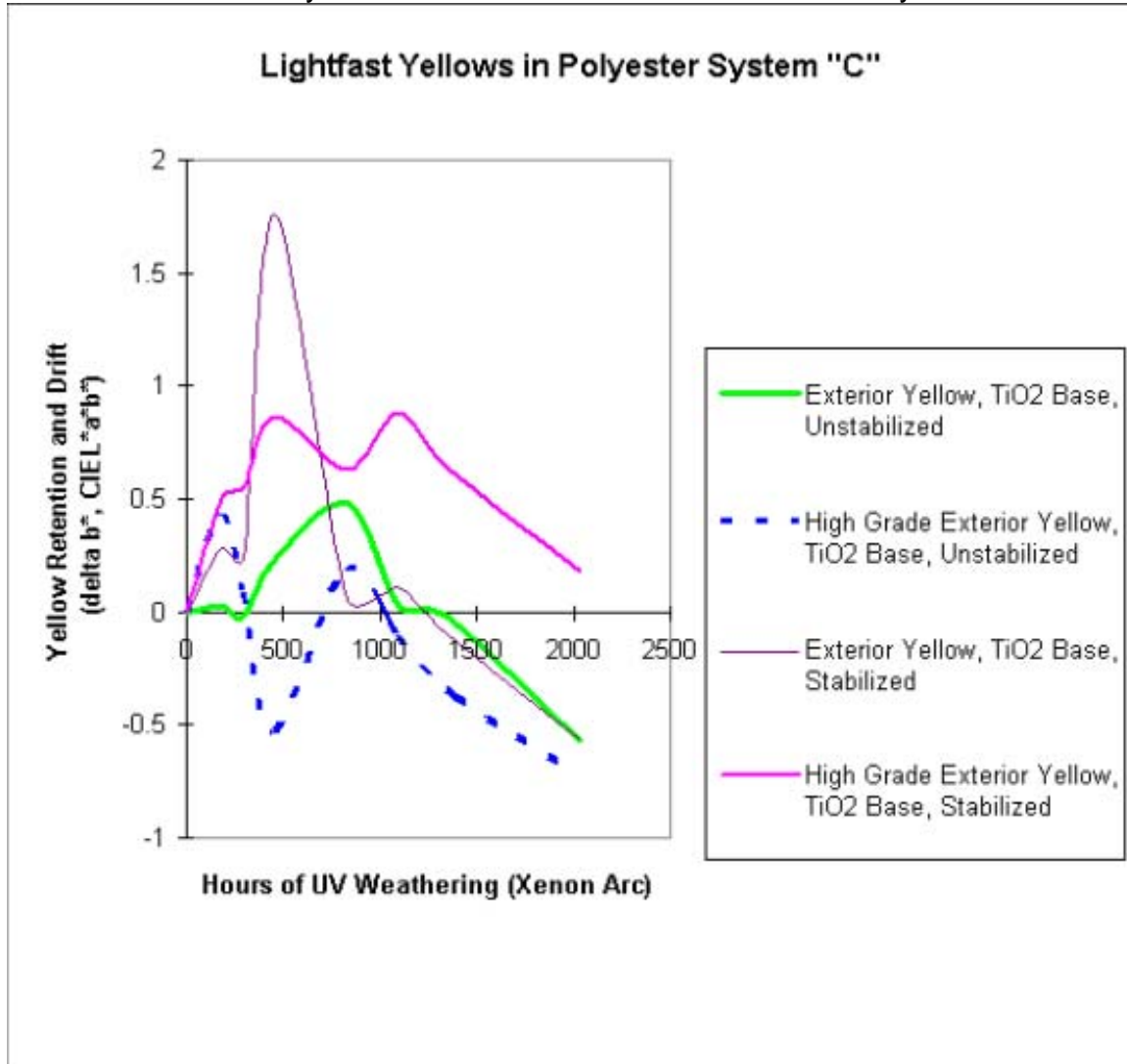
Table 7 shows drift in brightness as measured on the L\* scale of CIEL\*a\*b\* color space. Here, visible color change occurs in single colorant packages, as a darkening effect which dulls the color, and is shown in the table as a loss over time in L\* value. With multi-color reds, chalking and/or fade in red colorant quality shows as gain in L\* value, or in the presence of carbon black, darkening and dulling. In the case of these red epoxy composites, there was little benefit found to be gained from using the improved colorant. Why are these results so different from Table 6? The difference is the light-fastness of polymer that is used in making the composite. Color change resulting from decomposition of polymer is competing with color change inherent to the colorant.

Table 8. Degradation of Interior Grade Yellows in Polyester System "C".



The use of stabilizers had little effect upon the performance of interior grade yellow colors in System "C." How about exterior grade yellows?

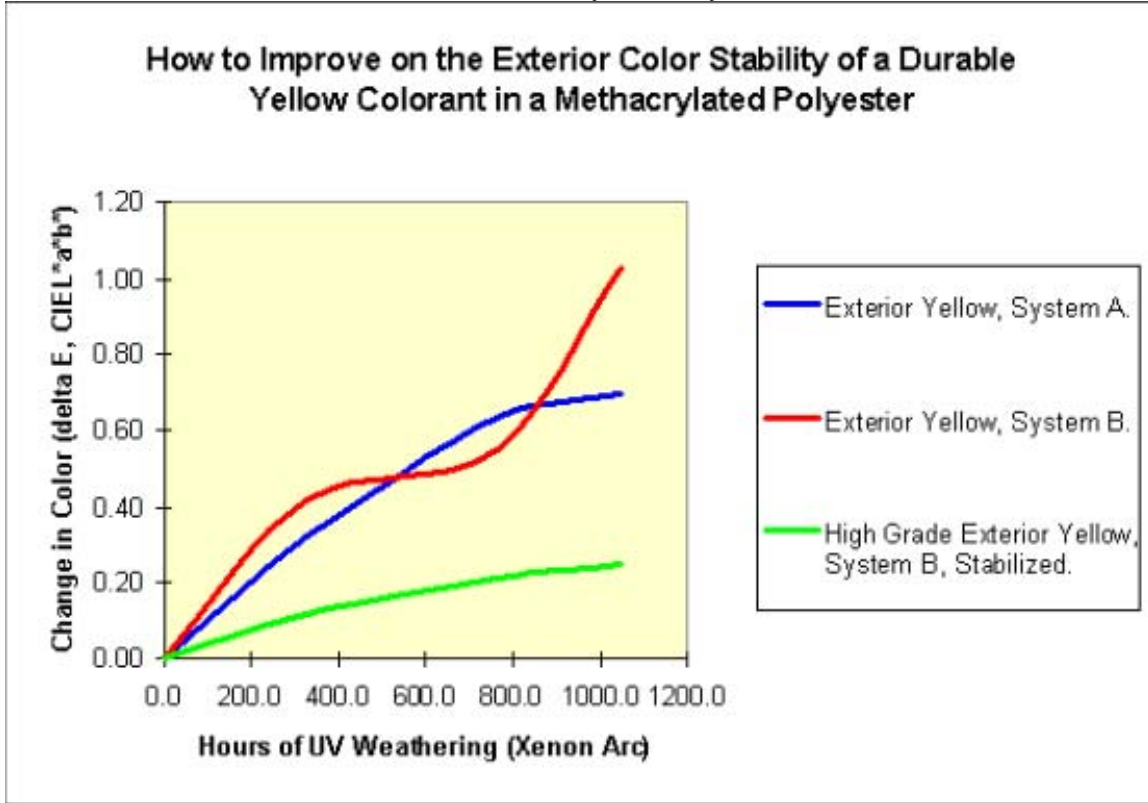
Table 9. Color Stability of Exterior Grade Yellow Colorants in Polyester "C".



A highly sensitive way to measure colorfastness of durable yellow composites is through the  $b^*$  scale of CIEL\*a\*b\* color space. In this color space, positive delta  $b^*$  indicates that the color has not visually changed. On this scale, loss of less than 0.5 delta  $b^*$  is also indication of success. It is not surprising that color change of exterior grade yellow colorants was orders of magnitude below what was seen with interior grades; however, the use of zinc sulfide as a tint base did not result in decreased color fastness when used with the highest quality yellow colorant and stabilizer. Is it possible that the high grade exterior pigments of this color space, with stabilizers, can enhance long-term stability in composites?

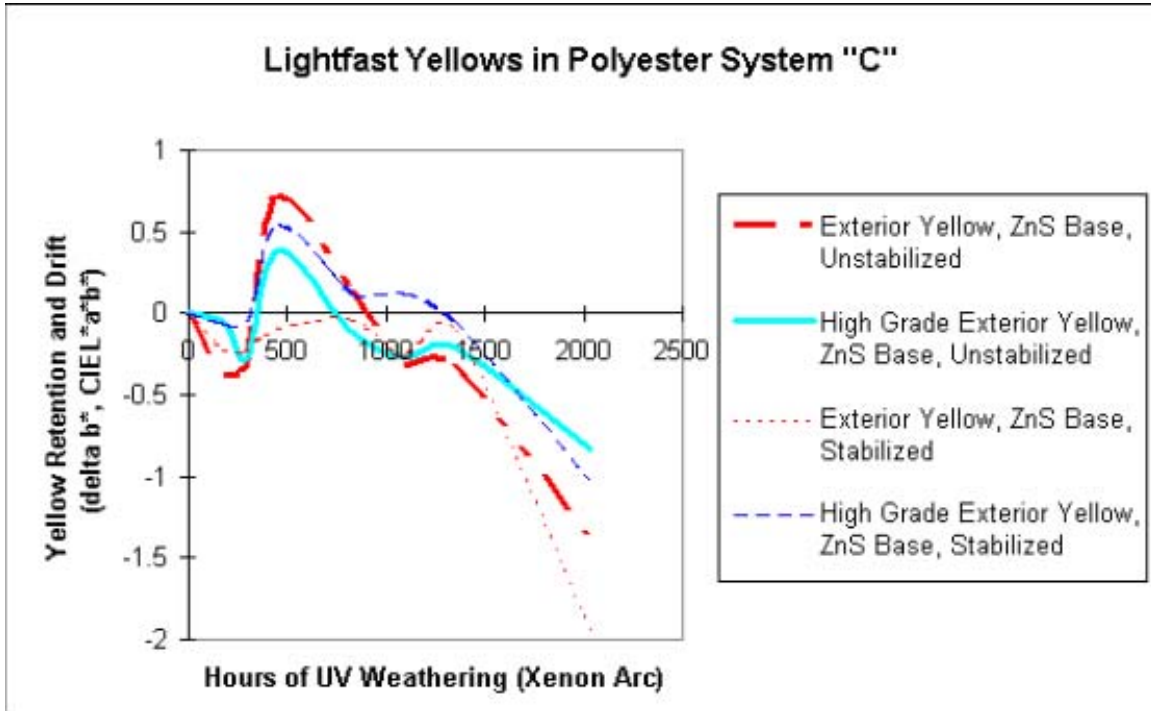
Examination of these same colorants as used in Systems A and C can help with this dilemma.

Table 10. Exterior-Grade Colorants in Polyester Systems "A" and "B".



The exterior-grade yellow in Table 10 represents an established standard for exterior performance in yellow composites. This yellow pigment, used in a system of strong lightfastness, is expected to provide strong performance, and our results concurred with this (see above blue line). Naturally, if the same exterior colorant is used in a polymer composite of lesser durability -- in this case, a styrenated polyester (see above red line) -- color stability suffers by comparison. Of course, if a better colorant or more stable system is found, it becomes possible to improve upon the standard, but that is not what is significant about these results. Our findings showed that it is possible to use a high grade colorant and stabilizer package to provide the highest levels of color constancy in a heavily styrenated polyester. As Table 10 shows, System "B" does not provide superior colorfastness to System "A" in this color space; the improvement, therefore, is provided by the colorant/stabilizer package.

Table 11. Zinc Sulfide as a White Base for Exterior Yellows



Comparison of Tables 9 and 11 suggests that it is possible for zinc sulfide to work well as an exterior tint base under certain specific conditions. How does this colorant compare to titanium dioxide, and what effect do white colorants have upon the color constancy of the system?

Table 12. White Colorants and Neutral Systems.

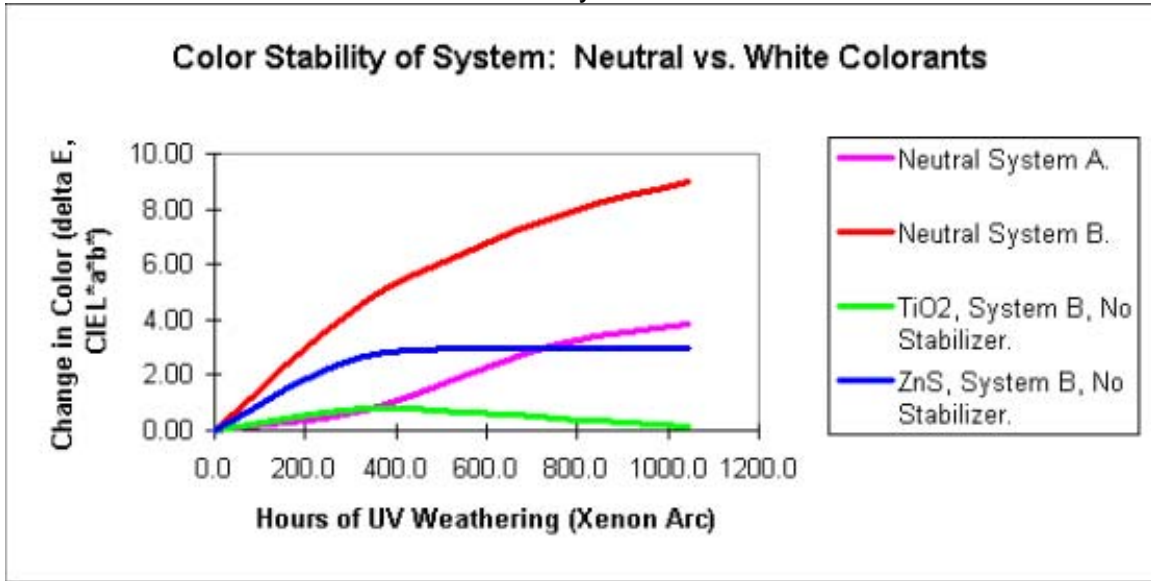
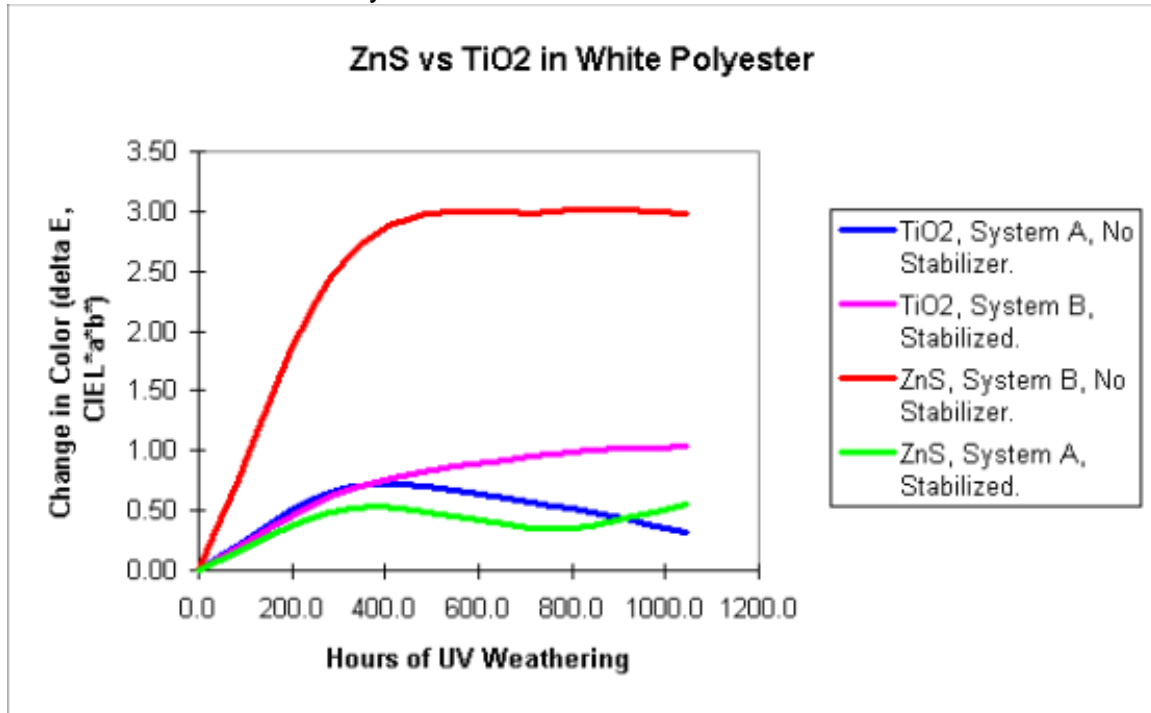


Table 12 offers some insights into system discoloration. System B is more prone to discolor than System A because of polystyrene modification (polystyrene yellows when exposed to UV radiation). Coloring this system with one percent white, zinc sulfide or titanium dioxide, has a marked impact in reducing discoloration. Of the two, titanium dioxide is notably more potent.

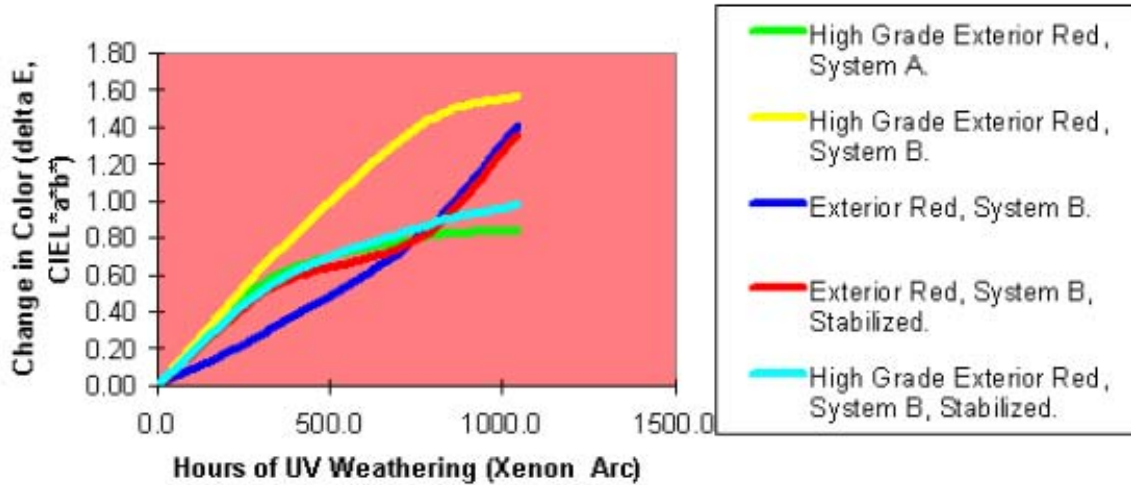
Table 13. Color Constancy of White Colorants.



As Table 13 illustrates, zinc sulfide can provide strong color constancy when used in a system of inherently good durability. In this context, titanium dioxide was found to be advantageous for obtaining good color performance in a broader range of compounds. However, it is very possible for compounders using wear and shear sensitive processes to achieve good stability with the appropriate use of resins, colorants, and stabilizers. These rules apply to other colorants.

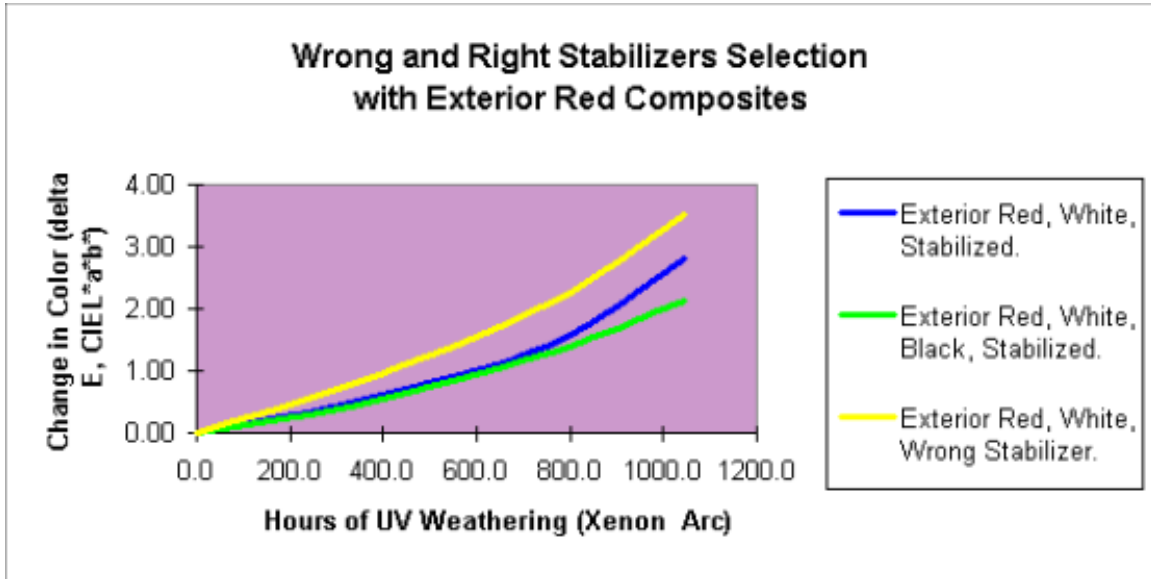
In Table 6, differences in exterior grade red pigments resulted in clear differences of performance. However, the polymer needs to be considered, and possibly, the stabilizers. Tables 14 through 16 offer some insights into what can happen when the wrong decision is made.

Table 14. Degradation of Systems "A" and "B" Red Single-Colored Composites  
**Red Colorants, Stabilizers, and the Polyester System.**



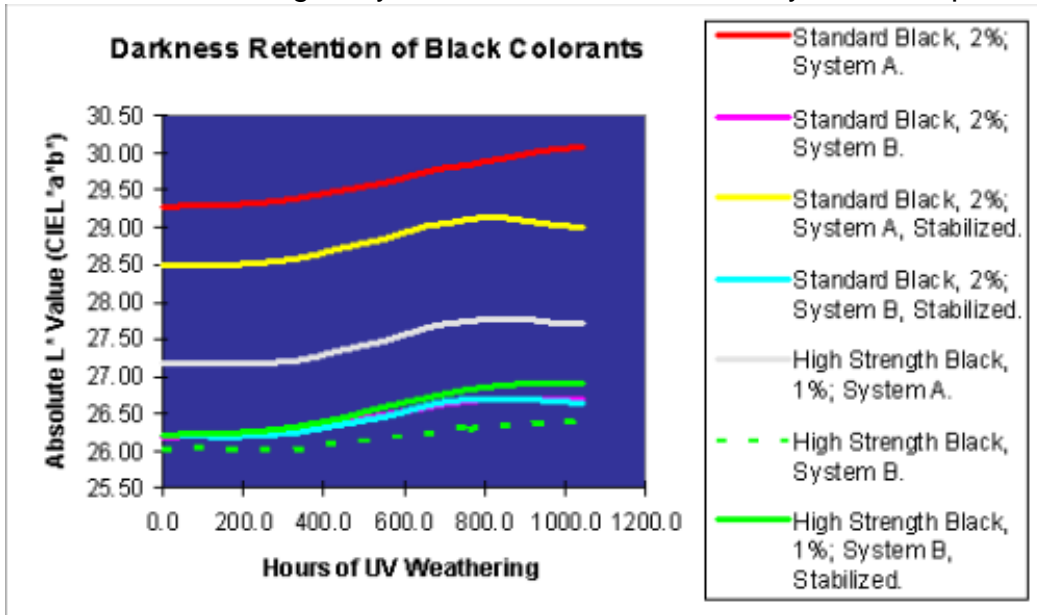
In Table 14, a high grade colorant exhibited strong stability in a system of high quality (see green line). However, it can be a mistake to expect the same performance from that colorant when used with a resin of lesser durability (see yellow line). Better productivity can be achieved by using more cost-effective colorant (dark blue line). On the other hand, if the application demands a styrenated system **and** strong colorfastness, a high grade pigment with stabilizers can provide it (see light blue line).

Table 15. An Exterior Red Composite, in System B, with White and Black Tint



As Table 15 demonstrates, addition of white tint does not improve the stability of this red exterior colorant, in a system of inherent vulnerability to ultraviolet light. While the presence of white is often necessary, using the wrong stabilizer is an expensive mistake to make (compare yellow and blue lines). Of course, there is always a fail safe. Minute amounts of carbon black can provide significant boost to stability, while retaining favorable rose-colored appearance. However, use of the wrong resin with carbon black can also have pitfalls (see Table 16).

Table 16. Weathering of Systems "A" and "B" Black Polyester Composites



In polyester systems possessing of low color value (e.g. black tones), improved polymer stability does not guarantee improved jetness over time. Table 16 shows the L\* values (CIEL\*a\*b\*) of black composites, as changing with UV exposure. Darker color (i.e., lower L\* value) is associated with less drift in darkness level, and is achieved in System B. In this case, the better polymer system failed to provide superior performance.

## V. Experimental.

All samples studied in this work were evaluated using an Atlas Model 65-WR Weatherometer, running Miami/South Florida humidity cycling. Although this instrument is not controlled irradiance, approximately 1000 hours of weathering, is considered to be the equivalent of a one year exposure in southern Florida.

Color readings were taken on a Datacolor International CS-5 spectrophotometer, using CIEL\*a\*b\* color space. Each sample consisted of two halves of the same molded part: a weathered sample, and a color standard stored in a cool, dark, laboratory environment. Practice for generating color readings consisted of following manufacturer recommended practices, including calibration of the instrument before use, and taking three color readings of the standard, followed by the same number of readings on the sample. All data presented was collected through this practice, although it was necessary to read certain samples (primarily urethanes) using small surface area view due to physical sample limitations.

In general, any sample evaluated was tested within the parameters of a particular control, at the same time, or over an extended period of time using multiple trials, to determine reproducibility. The urethanes in particular represented data from numerative designs of experiments beginning in January, 1995, and ending October, 1995. Urethane research employed a generic urethane system possessing an A:B side ratio of 2.21 to 1.0, with 134a type foaming agent, molded to a specific gravity of between 0.5 and 0.7. This phase of the study, covering hundreds of samples, with one or more duplicates of each trial, and several control populations consisting of three or more (usually six) samples, consisted of five distinct generations of study, each of which ran a minimum 1100 hours (as needed) in Miami cycle weathering in order to differentiate among experimental variations. Data on the white samples in particular was collected in two design experiments: 1) a fifty sample, 2000 hour trial from May until August of 1995, with a control population of twelve; 2) a thirty two sample, 1400 hour trial from July until October, with a control population of six. Based upon statistical percent confidence evaluations of these control populations, reproducibility of color change at the 95% level of confidence was found to be within 0.3 delta (Cielab) of the sample for any given trial.

Polyester variations were evaluated in the following formulas:

**System A**

Unsaturated Polyester Resin "A"	330.00 grams
35% Solids Methyl Methacrylate LPA	120.00 grams
tBPB Initiator	5.25 grams
Zinc Stearate	18.75 grams
Aluminum Trihydrate SB-432, Huber	1014.00 grams

**System B**

Unsaturated Polyester Resin "B"	550.00 grams
35% solids Polystyrene LPA	200.00 grams
tBPB Initiator	8.75 grams
Zinc Stearate	31.25 grams
Aluminum Trihydrate SB-432, Huber	1690.00 grams

**System C**

Unsaturated Polyester Resin "C"	381.28 grams
tBPB Initiator	4.78 grams
10% Inhibitor (4-t-butyl catechol) in Styrene	1.50 grams
Microthene FN-510	28.71 grams
Zinc Stearate	9.57 grams
Calcium carbonate	574.16 grams

For any given trial, fifty grams of polyester system were weighed into a six ounce cup, and colorant and/or stabilizer additions were made, using the quantity specified in the above tables. The system was then mixed at high speed, using an air-mixer with a marine blade. When the mixture was uniformly colored, it was poured onto a coarse fiberglass gauze patch. The patch was then sandwiched between double layers of fine fiberglass veil, and molded under pressure for two and a half minutes at 300 degrees Fahrenheit. The result of this procedure was a four inch wide square (about 1/8" thick), which was split into two four inch by two inch sections, for the color standard, and weathering sample, for this phase of our study.

The epoxy composite of this study was a two component thermoset. Part A consisted of:

DER-331, from Dow Chemical Corporation	985.00 grams
Byk A-515, from Byk Chemie	5.00 grams
PTG Cab-o-sil, from Cabot Corporation	10.00 grams

To fifty grams of Part A were added the amounts of colorant and stabilizer that are specified in the above tables. The combined suspension was mixed at high speed for sixty seconds, and 4.75 grams of DEH 24 were added as a curative. Again, the sample solution was mixed for sixty seconds. When a homogenous mixture of dispersion, epoxy-side, and curative was obtained, the sample was poured in even amounts into two analytically clean, 2 1/2" diameter, aluminum dishes, and cured for twenty minutes at 135 degrees Fahrenheit. When the samples cured, the aluminum was removed from the casting, resulting in the weathering sample and color standard for this series of experiments. These specimens consisted of 1/4" thick plaques.

Samples for all evaluations were allowed to equilibrate at room temperature (73 - 78 degrees Fahrenheit) for twenty four hours after molding, to ensure that post-cure effects did not interfere with our results. The conclusions from our findings are as follows.

## **VI. Conclusions.**

A notable colorant effect is noted when comparing black and white epoxies and urethanes, in Tables 1 through 4. As stated earlier, stabilized blacks of the species undergo far less color drift and are generally more stable than their white counterparts. Proper selection of colorant grades and stabilizers, has in certain

instances extended projected composite longevity by multiples of hundreds of percents. While this effect is less obvious in epoxies than in urethanes, an examination of the drift in lightness ( $L^*$ ) values in Table 4 provides significant information about the degree and type of degradation occurring in black epoxies. The unstabilized black epoxy exhibits twice the overall drift as its stabilized, high strength counterparts. The percent surface retention, after double-wiping with acetone, is indicative of the chemical integrity remaining to the epoxy composite after an equivalent two year southern Florida exterior exposure. Our best dispersion achieved 80% surface retention after one double wipe of acetone; this optimized colorant was also observed to achieve outstanding performance in the urethane system.

Our results demonstrated some inconsistencies with conventional color theory. For instance, in styrenated polyesters as well as epoxies, a red colorant of lesser quality exhibited equal or superior performance to pigments of greater inherent durability. This contradicts the tenet of color science that a more lightfast colorant will produce greater color stability. However, this discrepancy can be explained.

In systems of durability greater than the colorant, the colorfastness of the composite was determined by the colorant. On the other hand, when the polymer possessed equal or less stability (as measured by the tendency to form chemical changes that are visible in color) than the pigment, the color stability of the system was dictated by the rate of decomposition that occurred in the polymer. Consequently, we conclude that it is wise to consider the resin when selecting a colorant. A superior colorant is often wasted when the polymer itself is changing color dramatically. Our work in red color spaces illustrated this.

On the other hand, it was possible for a high grade exterior yellow to demonstrate remarkable colorfastness in a styrenated polyester. One factor influencing this is that visible absorptions associated with polymeric decomposition do not impinge upon the reflective properties of yellow pigments. These findings, collectively, constitute evidence of color-science based synergism between colorants and stabilizers, that is effective in a plurality of system chemistries.

It makes sense that for best results, one should select a pigment of durability slightly greater than that of the base polymer, and then stabilize the polymer. As it is wise to think about resin when selecting the colorant, it is just as valid to include principles of color science, in the selection of the stabilizer. Relationships between colorants, stabilizers, and polymers, often define the exterior lifespan of a composite. As Tables 14 through 16 illustrated, improper selection of any one of these ingredients can lead to premature failure. In making a decision for one ingredient, it is best to consider the properties of all three.