

# The Color-Dependent Characteristics of Weatherable Thermoset Composites

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## I. Introduction.

Over the course of the past decade, the exterior performance of fiberglass reinforced thermoset polyester compound has made significant progress in both technical performance, and acceptance within industry. As an example, there are several automotive original equipment manufacturers (OEMs) that have approved of, and are seriously considering, the use of black molded-in-color composites on the exterior of their vehicles – with no paint. Advances in formulation, process control, UV stabilization, and appearance science have made this possible. But what is required for SMC to take the next step is to produce composites of varied colors.

Principles of appearance science predict that a formulation found to be weatherable in one color, will not prove equally weatherable in a color of differing spectrophotometric characteristics and physical properties. In this paper, we examine six notable color spaces of significance and analyze their relative weathering failure modes in three polyester composite formulations, in an effort to prove or disprove this hypothesis. In process, some pitfalls of composite formulation are identified, and recommendations are made with respect to the further development of light-fast formulations.

## II. Scope and Experimental.

The work of this study encompasses three (3) color spaces: black, white, and yellow. The student of art and/or color science will note that black and white are opposites. These were chosen to compare and contrast with each other. Yellow was chosen, to compare and contrast with white and black, and because yellow is a color space that has proven to pose intrinsic difficulties to science and industry.

By selecting these colors, and by utilizing fundamentally sound colorants, We believe that several principles of formulating for exterior composites may be derived. Additionally, it was decided that in each of the three color spaces, we would use standard “CM” or “CF” colorants, versus colorants that have been modified for improved weathering performance (“UVS” colorants), to illustrate a few of the benefits and features of UV stabilization, coupled with appearance science.

Three composite formulations were included in this research:

1)	Experimental Polyester #1 (PG maleate)	38.1 %
	Polyethylene (low profile additive)	2.9 %
	Triganox C (initiator)	0.5 %
	Mod E (inhibitor)	0.1 %
	Zinc Stearate	1.0 %
	Calcium carbonate	57.4 %

2)	Experimental Polyester #1 (PG maleate)	38.1 %
	Polyethylene (low profile additive)	2.9 %
	Triganox C (initiator)	0.5 %
	Mod E (inhibitor)	0.1 %
	Zinc Stearate	1.0 %
	Aluminium trihydrate (ATH filler)	57.4 %
3)	Experimental Polyester #2 (proprietary chemistry)	25.4 %
	Experimental LPA #2 (proprietary chemistry)	13.6 %
	Triganox C (initiator)	0.6 %
	Mod E (inhibitor)	0.1 %
	Zinc Stearate	1.8 %
	Aluminium trihydrate (ATH filler)	58.5 %

For each trial, one hundred grams of polyester system were weighed into a six ounce cup, and constant concentrations (2%) of colorant were added. The system was then mixed at high speed with a marine blade. When the mixture was uniformly colored, it was poured onto a coarse fiberglass gauze patch and sandwiched between double layers of fine fiberglass veil. This resulted in a fiberglass-reinforced material of roughly fifteen percent (15%) glass by weight. We then molded the compound on a four-inch by four-inch mold, half textured, half untextured, for two and a half minutes at 300 degrees Fahrenheit, producing a four-inch wide square (about 1/8" thick). This was then cut into a two and a half-inch by four-inch rectangle, half of which was textured, for purposes of appearance measurement and accelerated weathering evaluation.

Appearance measurement, as it relates to this work, consisted of gloss and color measurement, performed on the glossy (non-textured) half only. All color readings were taken on a Gretag-Macbeth ColorEye 7000A spectrophotometer, using 10° observer, specular included, UV excluded, and are reported in CIEL\*a\*b\* (1976) color space. Gloss readings were taken via Byk-Gardner Micro-Tri-Gloss gloss meter, using 60° geometry. Calibration was performed prior to readings in agreement with manufacturer recommended practices; the numbers reported in this study constitute the average of three readings for any specimen at a given point in time.

Accelerated weathering was performed using an Atlas Model 65-WR Weather-O-Meter, modified using a 3-T rack with sample spray system (comparable to a Ci-65 Weather-O-Meter), with boro/quartz inner and outer filter, running Cam 186 for south Florida humidity cycling. This instrument is not a calibrated irradiance device; however, 1000 hours of weathering in this unit is historically equivalent to about one year of outdoor direct (5° south) exposure in south Florida. For all panels, appearance measurements were taken at the beginning of the test, at the end of the test, and at 500-hour increments of a 2000 hour (roughly two-year south Florida equivalent) accelerated weathering study.

This information considered, it is appropriate to move to our discussion of the color spaces and their results.

### III. Imperatives of Black, Low Color Formulations.

One of the things that is known to any art student, is that black is not a color. Rather, black consists of the absence of color. Because of this fact, principles of appearance science lead us to believe that photo-oxidative yellowing, for instance, will have negligible effect upon the weathering characteristics of a black composite. Surface erosion and chalking, however, may produce a dramatic effect (please see Figure 1).

*Figure 1. System 1 with 2% Plasticolors CF-20737 at 2000 hours xenon arc exposure.*



Figure 1 is a life-sized visual image of the panel made with 2% CF-20737 in System 1, after it has been exposed to 2000 hours of accelerated weathering via xenon arc Weather-O-Meter. Of significance, the areas near the left and right hand edges were covered by the holder, and were not exposed to the damaging effects of humidity combined with ultraviolet radiation; these areas retain their original color and appearance. The same cannot be said for the center of the panel, which has eroded, chalked, in some areas whitened, and generally lost its appearance. These failure modes, as demonstrated in Figure 1, are characteristic of polyester composites in black color spaces. In order to correct them, one must use the correct colorant and stabilizer packages to prevent surface erosion. But there is still more than this that needs to be done.

Figure 2 (please see following page) presents a life-sized image of the panel made with 2% UVS-20519, in System 3, following the same period of accelerated weathering. Unlike the panel presented in Figure 1, this panel has whitened somewhat, but retained its general surface characteristics and appearance – especially in the textured area shown in the upper third of the image. Of interest, this panel as weathered remains within 2.74 delta E\* (CIEL\*a\*b\*), and retains close to 44% of its gloss. This data leads one to predict that the above formulation is capable of surpassing automotive OEM tolerances for weatherability in south Florida; far more importantly, we have two-year south Florida weathering data collected on a similar, optimized formulation, that strongly supports this conclusion (see Table 1).

Figure 2. System 3 with 2% Plasticolors UVS-20519 at 2000 hours xenon arc exposure.



Table 1. Comparison of accelerated weathering results to an optimized formulation.

	% Gloss Retention	Color Difference, dE*	Test method
System 1, CF-20737	0.9		2.3 2000 hours xenon arc
System 2, UVS-20519	5.7		2.3 2000 hours xenon arc
System 3, UVS-20519	44		2.7 2000 hours xenon arc
Similar Optimized System	70		1.3 2 years south Florida

Regarding the above information, the discerning reader will note several important details. First of all, as predicted by principles of appearance science, the black panel from System 1 failed as a function of gloss reduction/chalking, and not color change. This is because black is the absence of color, and in the near absence of color, small differences in color are difficult to observe. Secondly, the reader will note that color change in the black panel from System 3 manifested as a white hazing in areas strongly correlated to the presence of glass. Thirdly, System 1 made use of calcium carbonate as filler; calcium carbonate is a chemistry that associated with several critical failure modes in UV resistant composites. From this information, we draw several conclusions about formulating to a black color space:

1. Do not formulate the system or UV package around minimizing color change, as color change is not the mechanism of weathering failure;
2. Use sufficient colorant and/or other techniques as to provide adequate coverage of glass;
3. Regardless of the color space, avoid calcium carbonate as filler when formulating to requirements of more than 500 hours xenon arc, or six months outdoor performance;
4. From experience, and from the published literature, we believe that xenon arc test methods are a reasonable predictor of actual outdoor weathering performance for the polyester composites of this study.

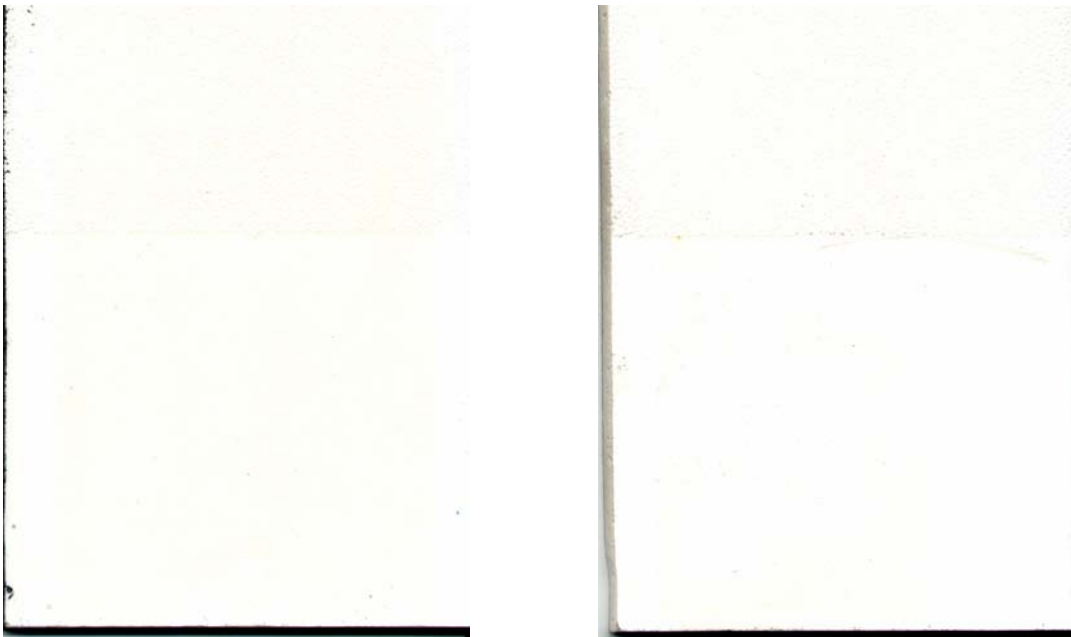
#### IV. White is the Presence of All Color.

Another thing that is known to any art student, is that white is not a color. In contrast to black, white is the presence of all colors. In color science, we refer to white color spaces, and other colors of intense luminosity, as “high color.” But what is important to remember about white formulations, is that color change is visible (please see Figures 3 and 4, below).

*Figure 3. CM-1004 (left) vs. UVS-10287 (right) in System 1; all panels shown as after 2000 hours xenon arc exposure.*



*Figure 4. CM-1004 (left) vs. UVS-10287 (right) in System 2; all panels shown as after 2000 hours xenon arc exposure.*



A known problem of formulating a white exterior thermoset composite, is that most resin systems contain significant amounts of styrene and/or other aromatic chemistries that discolor upon exposure to sunlight. Figure 5 illustrates two of the most severe color changes observed, while Figure 2 illustrates two of the least severe changes. In this particular color space, color change of more than two units ( $\Delta E^*$ , CIEL\*a\*b\*) is often considered to be objectionable, whereas color change of less than one unit can scarcely be seen.

Figure 5. Color drift of White composites upon xenon arc exposure.

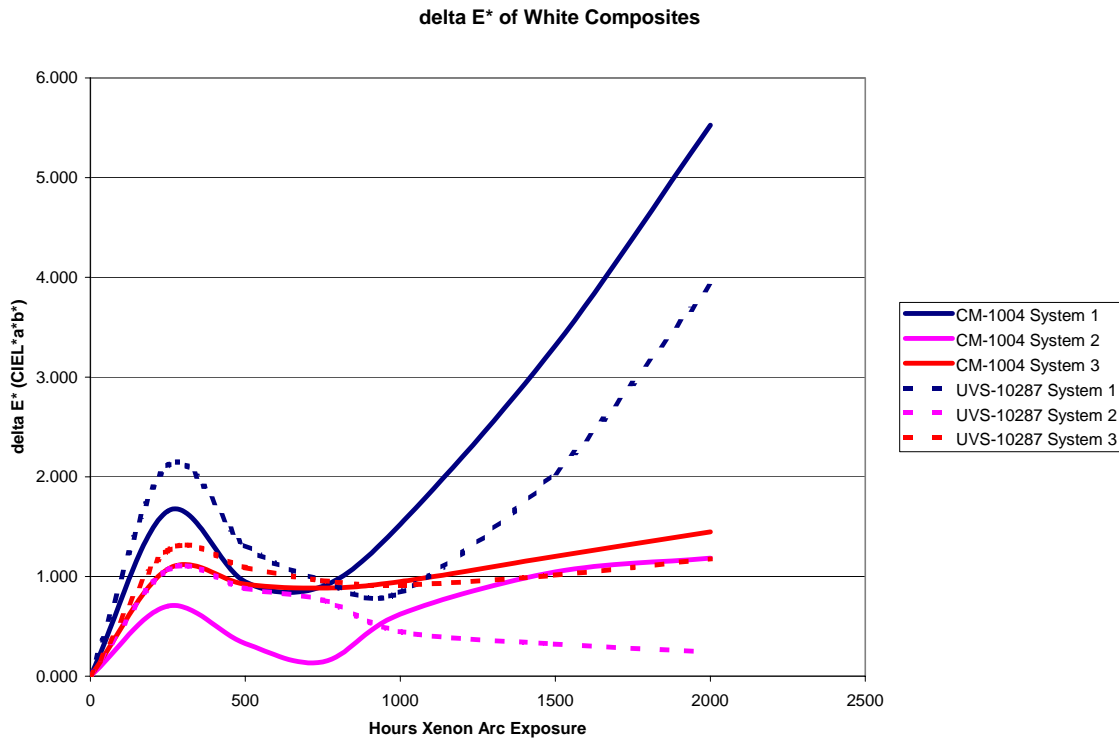


Figure 5 is a diagram illustrating the numerical values associated with color change shown in the previous figures. The x-axis of this diagram plots time of UV exposure, while the y-axis denotes units of color change in  $\Delta E^*$  CIEL\*a\*b\*. An interesting phenomenon of white composites is that color change transpires rapidly in the first two hundred hours of xenon arc exposure, and after that, the color difference appears to reverse direction and improve. To some, this might seem to indicate the probability that weathering of composites can improve their appearance, or that degradation of such materials can be reversed. Let us reassure the reader that this is not the case in this instance.

In a high color composite application, there are two major features of UV degradation. One of these features is the discoloration that is so readily observed and objected to in Figure 3; the other feature is that of chalking and surface erosion, in which physical damage to the substrate causes the composite surface to appear dull and white.

A white composite that gains whiteness is not likely to lead to objectionable appearance. But if surface erosion causes the substrate to look extremely dull or chalked, or if it proceeds to the point that glass – normally imbedded and hidden beneath the surface – becomes exposed, we can have a phenomenon that is extremely objectionable. The term for this phenomenon is “glass fiber bloom.” Alternatively, if a white composite discolors, then change in appearance is readily identified and objected to by most observers. In white color spaces, fiberglass composite formulation must guard against not one, but two separate and distinct modes of degradation that can lead to objectionable appearance.

These imperatives contrast sharply to those of the black color space, in which we have seen that the impact of raw color change is comparatively small, and that chalking and surface erosion leads to objectionable appearance. But there is another comparison to be made.

In Table 1, we summarized the weathering data of several systems and colorants, and compared System 3 to a formulation of similar chemistry that had been weathered for two years in south Florida. The chemistry and colorants used in System 3 dramatically outperformed those used in Systems 1 and 2. A novice in the practice of formulating weatherable compound might be inclined to look at this data, and attempt to formulate other colors of composite using the chemistry of System 3. As we have shown, that assumption would be a mistake; the best performing chemistry in our white color space was System 2 with UVS-10287. Of significance, UVS-10287 contains significant quantities of titanium dioxide pigment and UV stabilizing additives that are effective at curbing the degradation mechanisms inherent to System 2. Because of this fact, it was possible in this instance to take a system of lesser inherent weatherability, and convert into a system of greater weatherability for this study. Having the most expensive, most weatherable ingredients is not as important as having the correct system components for the color space, colorant, and application. What is perhaps of even greater importance, is to have all of these items working together in complementary fashion.

Having examined both the white and the black color spaces, we turn our attention to the outlying color regions, beginning with yellow.

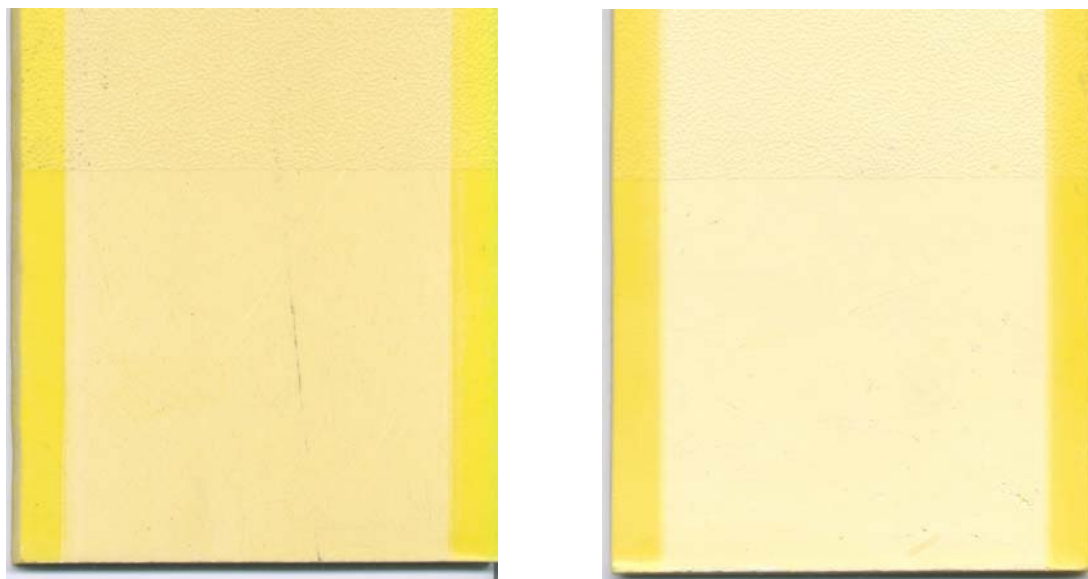
## **V. Bright Organic Yellow.**

For decades, yellow has been a sore spot for composites and coatings, noted for poor weatherability. One of the reasons for this reputation is that the chromophores used to formulate organic yellow pigments must by definition absorb ultraviolet light; it is the process of absorbing ultraviolet energy that damages the pigment and destroys the color.

Another, equally important reason, is cost. Compared to titanium dioxide (white pigment), and carbon black (black pigment), organic yellow colorants are extraordinarily expensive, especially for a type of colorant that possesses a modicum of UV lightfastness. For this reason, to fabricate yellow composites, compounders have used colorants that are very strong, and they also have used less of them than of white or black colorants. Consumers, in turn, came to expect little exterior colorfastness from molded parts in this color space, understanding that there was little that could be done.

For purposes of this study, we selected a colorant of relatively strong inherent lightfastness, that for decades was state-of-the-art in industry, in order to best illustrate the dilemma. A review of Figure 6 captures the problem very nicely.

*Figure 6. Plasticolors CM-80373 in System 1 (left) and System 3 (right); all panels shown following 2000 hours exposure in a xenon arc chamber.*



Given what we have said about (a) yellow colorants, and (b) the use of calcium carbonate as a filler, it should come as no surprise that System 1 with CM-80372 would exhibit chalking and dulling of the colorant following 2000 hours of xenon arc exposure. But what is surprising is that a colorant of strong inherent lightfastness would demonstrate notoriously worse performance when used in a system (System 3) of demonstrably superior inherent weathering characteristics to those of System 1. Since the 1970's, this is exactly the problem that industry faced with respect to the yellow color space:

If a compounder used an interior grade yellow colorant in an economical, calcium carbonate filled system, one expected relatively poor lightfastness. But if one went to the trouble to use a high quality colorant in a system of supposedly superior lightfastness, one would expect to achieve some improvement in weathering performance – and as we have demonstrated, this wasn't at all the case in many instances. This is a phenomenon that was not understood nor addressed until research in the mid-1990's began to shed some light on the dilemma. Fortunately, with the assistance of appearance science methodology, we are now in a position to explain and resolve the technical issue.

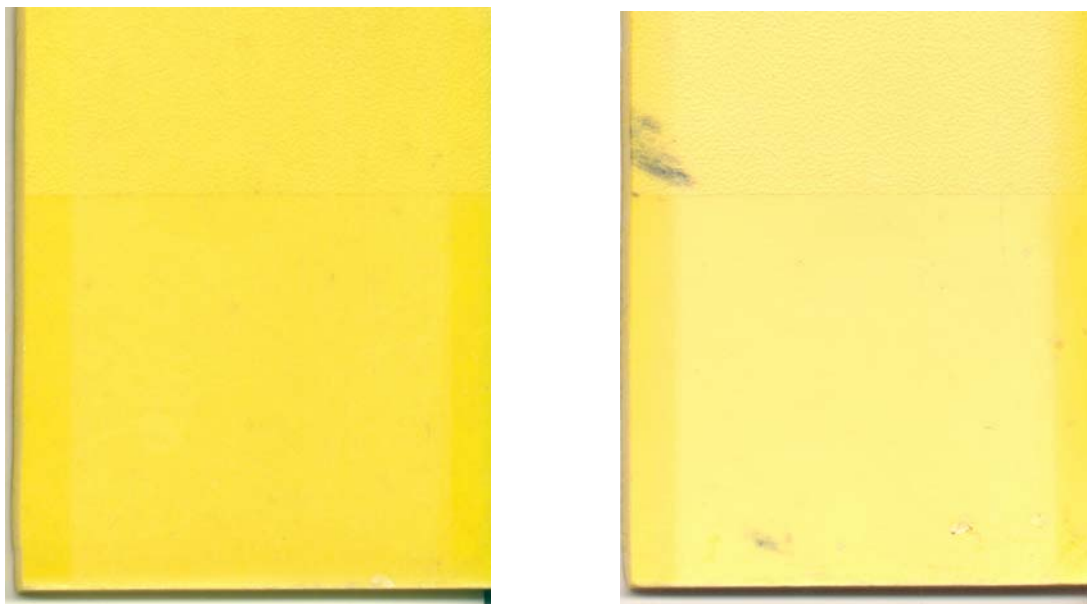
In color science, we achieve a bright yellow color in molded composites by subtracting out the reflection of blue light back to the observer. This is what a yellow pigment does: it absorbs the higher energy (i.e. blue and green) wavelengths of visible light, while allowing the lower energy wavelengths (yellow and red) to be reflected back to the observer. As we have suggested previously, even a high-performance organic yellow colorant possesses a certain degree of

susceptibility to UV degradation. This is a function of the fact that its chromophore must absorb ultraviolet energy in order to absorb the blue wavelengths that give the pigment with its color. Now let's apply what this means to systems of lesser and greater inherent durability.

In any polymer or composite matrix, we expect that damaging ultraviolet energies must pass through the surface of the system – through the polymer – before they can reach the pigment. In a system of lesser durability, this energy will be damage the polymer – and thus be absorbed – before it has a chance to damage the pigment. In this manner, principles of appearance science predict that inherent lightfastness issues associated with the colorant itself will be blurred and obscured from the observer by the chalking, yellowing, and degradation of the polymer matrix. In a system of superior inherent lightfastness, we expect that a greater quantity of damaging ultraviolet energy will be able to reach the pigment without being absorbed. This, we would predict, should result in all of the inherent vulnerabilities of the colorant being exposed..

This is the source of the dilemma that we have already described. The inherent properties of organic yellow colorants introduces an element of vulnerability to systems of greater and lesser durability, thus causing both systems to degrade more rapidly than they otherwise would. Fortunately, these principles of appearance science that lead us to the source of the problem also point to a solution, which we demonstrate in Figure 7. Naturally, we will have to get rid of the calcium carbonate filler, but we believe that with proper UV stabilization of the pigment, the selected system chemistries are capable of providing satisfactory performance.

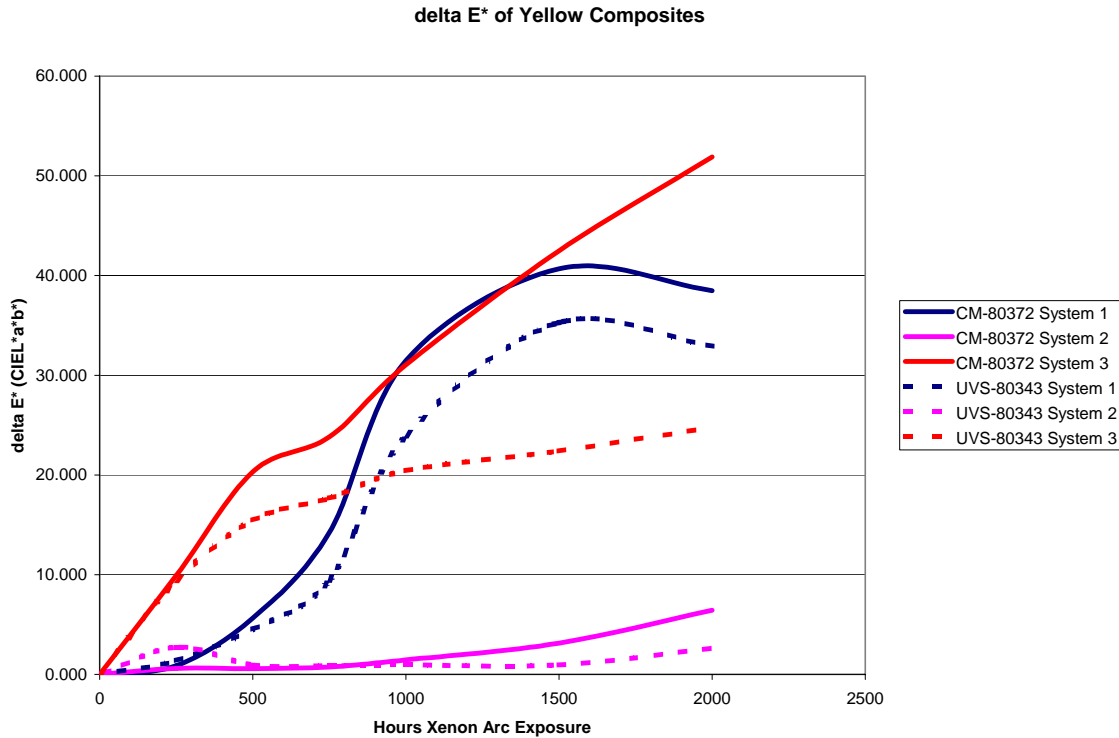
*Figure 7. Plasticolors UVS-80343 in System 2 (left) and System 3 (right); all panels shown following 2000 hours exposure in a xenon arc chamber.*



*\*-Note: the blemishes in the upper left and bottom of the right-hand panel are molding defects, not related to weatherability. While of academic interest, they are not relevant to this work.*

As we would expect, UV stabilization of the pigment, coupled with replacement of calcium carbonate as filler, leads to dramatically improved weatherability. Numerical values for these results are shown in Figure 8.

Figure 8. Color drift of Yellow composites upon xenon arc exposure.



The reader will note that the above diagram is similar to that of Figure 5, which in a like manner, plotted color differences of white composites across two thousand hours of weathering. A major difference exists, however, in the scale of the x-axis. In the yellow color space, chalking and faded yellow panels are changing by entire orders of magnitude. The reader should also note that while the color constancy of System 3 was dramatically improved, it did not achieve the level of acceptability shown in System 2. This is because certain system chemistries work very well in conjunction with certain pigments, and vice versa. We believe that in a yellow color space, System 3 can be improved to match or even better System 2 with UVS-80343 by selecting a more lightfast colorant. This begs the question of why one would want to do so, however, when the performance of System 2 with UVS-80343 is already acceptable – and at reduced relative cost to the consumer.

System 3 is a low shrink formulation, whereas System 2 is not. If a consumer is looking for a Class A finish, or low shrink performance in their application, this imperative is likely to detract from the economics, and/or color uniformity and weatherability of the overall compound. Color uniformity, incidentally, is a requisite to a compound that is also weatherable; a compound that appears mottled when molded, will not improve in its appearance following exposure to sunlight and/or other damaging elements.

## **VI. Conclusions.**

There are two important issues that are addressed in this work. In the yellow color space, we have seen that a less than optimal colorant can achieve optimal performance in a less than optimal system. For reasons that have been addressed, this same colorant has been shown to fail when employed in a system of theoretically superior lightfastness.

In the white color space, we have seen that a small amount of chalking and/or surface erosion can be beneficial to the short-term appearance of a white composite substrate. And in the black color space, we have seen that this same chalking and/or surface erosion can lead to weatherability failure. But these observations merely touch upon the surface of a far deeper and more important issue.

It is easy to make the assumption that once one has developed a stable formulation, one can always change colors and colorants, and so long as those colorants themselves are stable, retain the lightfast properties of the superior formulation. Unfortunately, this assumption is very often a mistake. A formulator, for instance, who develops our yellow System 2, and then attempts to reformulate the same system into a black application, is headed for failure. Similarly, a formulator who first develops black System 3, and then tries to apply this to the white or yellow color space, is not likely to be pleased with the results. And these are just two examples. Like most things that we put into our formulations, colorants are chemicals, and like other chemicals, have interactions with sunlight and/or other chemicals that are often unique.

Principles of appearance science lead us to believe that the imperatives of weathering degradation are unique for every color space. Moreover, because every colorant has unique chemistry, and unique interaction with other chemicals, a change of colorant within the exact same color space can affect how the overall matrix will respond. When formulating a reinforced composite material, it is a good idea to have some idea of the behavior of the polymers, and the of the pigment chemistries – and most importantly, to understand how these chemistries will interact with one another.