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VOC Reduction and UV Stability of New Engineering Resins

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VOC Reduction and UV Stability of New Engineering Resins

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Abstract

Trends in styling continue to include metallic accents traditionally coming from paints and chrome plating. While paint and plating allow designers to achieve this desired look, both processes come with relatively high cost and are not environmentally friendly. VOCs (volatile organic compounds), chemical disposal, and no potential to recycle once the part is painted or plated are environmental concerns. In addition to wanting to eliminate VOCs from the painting process, there are new requirements for reductions in VOCs in the interior automotive cabin. New engineering resins have been developed which eliminate the need for painting and help to reduce interior VOCs. The UV stability of this solution is a potential concern when using traditional accelerated methods. This article looks at developing these resins and overcoming any UV stability concerns.

Background

Some resins, including engineering resins, require a secondary operation post molding to achieve the required aesthetics for appearance applications. The secondary operation could be painting or plating, for example, and this may include multiple steps to achieve the desired function and appearance. These secondary operations are required for a number of reasons, including:

- the desired color is not achievable in the resin
- the desired color is achievable, but the surface has flaws
- the desired color is achievable, but the UV stability is poor
- the desired color is achievable, but the gloss is not correct (too high or too low)
- the desired effect color is not achievable in the resin (metallic, pearlescent, etc.)

If any of the above conditions are encountered, painting or plating is often proposed as a solution. The costs associated with these secondary operations can be somewhat complex to capture. Not only are there the obvious costs associated with the materials and application of the painting or plating, but there also can be one or more pre- or post-steps in the painting or plating process. Etching the surface, applying a primer, flame, plasma or gamma treatments, heat curing, top coats, and so on all add incremental cost to the process. Moreover, people seldom include solvent and other chemical disposal costs to the entire process. If surface defects are observed after painting or plating, scrap costs are higher than unpainted/unplated part costs. Once painted or plated, the part is no longer able to be reground or recycled, making the final part less environmentally “green.”

Table 1

UV Performance of Metallic UVPOM Copolymer Exposed using Solar Method ASTM G147 (GM 9538P)

Sample	Exposure Levels			
	30 kL	55 kL	80 kL	105 kL
Satin Chrome	0.58	0.97	1.21	0.89
Chrome 2	0.20	0.23	0.19	0.11
Silver 1	0.21	0.21	1.26	0.38
Silver 2	0.34	0.52	0.28	0.33
Zinc 1	0.20	0.96	0.99	0.20
Zinc 2	0.33	0.55	0.35	0.10

Table 2

UV Performance of Metallic UVPOM Copolymer Outdoor Direct Exposure SAE J1976

Satin Chrome Exposure	Florida DE*	Arizona DE*
1 year	1.51	1.38
2 years	1.50	1.72

Table 3

Target Compounds for Vehicle Air Quality

Compound	Target Range (µg/m ³)
Ethylbenzene	< 4,000
Xylene	< 900
Tetradecane	< 350
Toluene	< 270
Styrene	< 250
Dibutylphthalate	< 240
Diethylhexylphthalate	< 130
Formaldehyde	< 100
Acetaldehyde	< 50

Another drawback of using painting and plating as solutions is that they limit the number of potential resins for these applications. Many resins are not paintable or platable, and if the class of resins is, it is often through formulation modification which can further increase the cost of the base material even before the secondary operation is applied. It is much more desirable to solve these issues with resins, which can achieve the desired appearance right out of the mold without secondary operations.

Colorability, conventional UV stability, gloss control, and metallic effect colors were discussed at the SPE ANTEC® 2010 by the author [1]. In this article, we will focus on metallic resins to eliminate paint, test methods to determine volatile organic compounds (VOCs) for automotive interiors, formulation development to reduce those interior cabin VOCs, and UV testing issues and concerns with those formulations.

Metallic Molded-in-Color Eliminate VOCs from Painting

For the most part, painting and plating are the most common methods to achieve metallic finishes on appearance parts, particularly critical appearance parts like automotive interiors or appliances. Molded-in-metallic plastics were generally used for non-critical parts such as bottle caps, pen caps, disposable items, etc. Molded-in-color metallic plastics generally are characterized as having a duller metallic gray color, looking more sparkly than actually metal-like, and potentially having highly visible, very dark flow and weld lines depending on part geometry.

In acetal copolymer, work was undertaken to improve the appearance of molded-in-color metallic to reduce visible weld lines and increase the reflectance of the color. This was achieved through pigment technology, and mold design and processing. Aluminum pigments are typically available in three forms: cornflake, lenticular (silver dollar), and spherical. Cornflake pigments are characterized by a flat pigment geometry with an irregular edge. Lenticular pigments have flatter geometry with a smooth edge. Lenticular pigments are generally brighter than cornflakes due to the smoother flat surface. Brightness can be

further increased by polishing the aluminum pigments. Spherical pigments are round and contribute more sparkle effect than true metal effect.

Combining metallic flake considerations and optimum tool design, satin chrome appearances can be achieved which mimic the appearance of painted or plated parts. In acetal copolymer, toner pigments can also be

incorporated to achieve satin chrome, satin nickel, satin silver, and satin aluminum looks. These colors exhibit metallic brilliance with or without the speckled look. Flow and weld lines are still visible, but are not dark black in color, and typically are similar in color to the background so they are less objectionable.

UV stability of metallic colors is also important, both for interior automotive applications and for potential exterior applications, including automotive and non-automotive markets. In acetal copolymer, combining world-class UV technology with the metallic formulations provides molded- in-metallic colors that meet OEM requirements for interior automotive applications. Testing in the Atlas Xenon Arc Weather-Ometer® using test methods SAE J2412/J1885, Ford FLTM BO116 -01, and VW PV1303 all show excellent performance over a wide range of colors, with color difference values after exposure of less than 3.0 CIELab units and an AATCC gray scale rating of 4 or higher.

Table 4
Comparison of UV Test Methods

	General Motors, Chrysler, Others		Ford U.S.		VW	Honda	Toyota
Test Method	SAE J2412/1885		BO 116-01		PV1303	HESD6601	TSL0601G
Test Device	Xenon arc		Xenon arc		Xenon arc	Xenon arc	Xenon arc
Inner Lamp Filter	Quartz		Quartz		Borosilicate	Borosilicate	Borosilicate
Outer Lamp Filter	Borosilicate		Borosilicate		Soda Lime	Soda Lime	Soda Lime
Filter Lantern	None		SF-5		None	None	None
Exposure Energy	1,240.8 kJ/m ²		3,609.6 kJ/m ²		1,400 kJ/m ²	Varies	800 kJ/m ²
Exposure Time	ca 800 hrs		ca 1,200 hrs		ca 750 hrs 10 cycles	Varies	Up to 1000 hrs
Surface	Grain/stipple		Grain/stipple		Grained	Grained	High gloss
Wavelength	> 270 nm		> 335 nm		> 320 nm	> 320 nm	> 320 nm
Irradiation Control	@ 340 nm		@ 420 nm		@ 420 nm	@ 340 nm	@ 340 nm
Cycle	Light	Dark	Light	Dark	Light only	Light only	Light only
Irradiation	0.55 W/m ²	--	1.06 W/m ²	--	1.2 W/m ²	0.55 W/m ²	0.55 W/m ²
Black Panel Temp	89°C	38°C	89°C	38°C	n/a	89°C	89°C
Black Std Temp	n/a	n/a	n/a	n/a	100°C	n/a	n/a
Dry Bulb Temp	62°C	38°C	62°C	38°C	65°C	62°C	62°C
Relative Humidity	50%	95%	50%	95%	20%	50%	50%
Cycle Time	3.8 hrs	1.0hr	3.8 hrs	1.0hr	n/a	n/a	n/a
Referee Method	GM 9538P		None		None	None	None

To confirm performance in the field, outdoor accelerated aging was performed under glass using test method ASTM G147 (GM 9538P). This test utilizes a tracking box that tracks the sun’s trajectory in the Arizona sky with samples mounted below unglazed, laminated glass. Temperature in the box is not controlled, but had a maximum temperature reported as 102°C. Testing using this method was to a total exposure of 105 kL (kiloLangleys). All samples tested showed virtually no change after the 105 kL exposure. Data is shown in Table 1.

To complete the understanding of the UV performance of metallic acetal copolymer colors, satin chrome was exposed to direct sunlight in Florida and Arizona using test protocol SAE J1976. Direct exposure was conducted at an angle of 5° South on an open back rack. Testing has been completed for two years. Exposed samples show little change after two years of exposure in both climates. Color difference data is shown in Table 2.

Low VOC Formulations

Discussion up to this point has been focused on eliminating painting and plating for appearance parts. One of the drivers is to get “green” by eliminating VOCs from the painting process. For automotive interior applications, we can further get green by also reducing VOCs from materials used inside the vehicle. VOCs from materials contribute to the “new car smell” and potentially to fogging of windows. Most OEMs have had test methods and requirements to characterize fogging in place for many years.

Concern with interior vehicle air quality and subsequent testing began with European OEMs over 10 years ago. It is this author’s opinion that this concern was not related to any health risk, but rather trying to eliminate the new car smell in the interiors. This is further evident by the adoption of several qualitative smell tests such as VDA 270 from the German Association of the Automotive Industry. This test method deals with rating the odor of materials, with ratings such as “perceptible, not disturbing” and “very disturbing.”

Quantifying air quality in living spaces has gained momentum in Japan over the last decade. In Japan, the Ministry of Health, Labour and Welfare (MHLW) formulated indoor concentration guidelines for 13 VOCs due to “sick building syndrome.” The following quote defines sick building syndrome: “There have been numerous reports on residents of newly built or recently renovated houses and buildings suffering from physical disorders, due to the increased air tightness of houses and the use of building materials and interior finishing materials containing chemical substances which evaporate and contaminate the air in the rooms. While this phenomenon involves diverse symptoms, as well as the mechanisms such as the onset are largely unknown, and the factors are many and complex, such symptoms are generically called sick building syndrome.” [2]

The Japan Automobile Manufacturers Association (JAMA) viewed passenger compartments in cars as living spaces and voluntarily worked on defining and reducing vehicle cabin VOCs before legislation was handed down by the MHLW. JAMA’s voluntary action began with model year 2007. Other countries in Asia quickly followed Japan’s lead, including China and Korea. U.S. OEMs are evaluating as requirements expand to vehicles exported to those regions.

VOCs in auto cabins come from a variety of sources including plastic parts, carpet, seat coverings, foams, adhesives, leather, wood, insulation, and so forth. Specific compounds contributing to VOCs

include toluene, xylene, styrene, ethylbenzene, formaldehyde, vinyl monomers, etc. Note that each OEM will most likely have its own list of targeted compounds and levels. VOC testing for auto interiors is generally a three-tiered process. The most important requirement, and the one addressed by JAMA, is testing air quality at the vehicle level. In these tests, fully assembled vehicles are placed in a chamber, with interior air samples collected at the driver’s breath location and analyzed. Table 3 shows a list of the common compounds being targeted and typical levels for

Table 5

GM 9538P Solar Testing Versus Xenon Arc SAE J2412 Low Emission, UV Stabilized Acetal Copolymer Resin

Color	GM Code	GM 9538P 105kL	SAE J2412 1,240.8 kJ/m ²
Gray	310N	1.34 / pass	3.10 / fail visual
Gray	311N	0.53 / pass	2.57 / fail visual
Gray	312N	0.58 / pass	3.87 / fail visual
Gray	313N	0.58 / pass	2.35 / fail visual
Ivory	314N	0.81 / pass	2.41 / fail visual
Tan	830K	0.38 / pass	2.23 / fail visual
Tan	831K	0.54 / pass	3.16 / fail visual
Brown	413P	0.39 / pass	4.43 / fail visual
Blue	400G	2.86 / pass	2.50 / fail visual
Red	4592	0.60 / pass	4.75 / fail visual
Maroon	108D	2.30 / pass	8.81 / fail visual
Black	848	1.12 / pass	0.65 / fail visual

Requirement DE < 3 and pass visual*

vehicle level testing. Variables include temperature inside the vehicle, time at temperature, and sampling with or without ventilation.

The second level of testing is conducted at the component or part level. In this testing, the component or part is placed either in a chamber or a bag which is then heated. Samples of the headspace in the chamber or bag are collected and analyzed. A common chamber method test is VDA 276. A typical bag method is Japanese Automobile Standard (JASO) M902. In both methods, samples are heated at 65°C for 2 hours. Collected air is analyzed for VOCs.

The third tier of testing is at the material level. Here, tests such as VDA 277 (VOC by headspace GC) and VDA 278 (VOC by thermal desorption) are designed to measure the total VOCs from individual materials.

In the case of acetal resins, a specific test to measure formaldehyde emission is available as VDA 275 from the German Association of the Automotive Industry. In this test, two acetal injection molded specimens are suspended over water in a glass container. The water is present as it will absorb any formaldehyde emitted from the acetal resin. The container is heated in an oven for 3 hours at 60°C. After cooling, the water is analyzed for formaldehyde using the lutidine method, with results reported as ppm of formaldehyde.

Low Emission UV Stabilized Acetal Copolymer

We have shown so far that it is possible to eliminate paint VOCs and reduce vehicle cabin VOCs by using molded-in-metallic acetal copolymer. It is also important to reduce cabin VOCs for conventional colors in UV stable acetal copolymer. One would anticipate an easier task compared to molded-in-metallic, UV stabilized, low emission acetal copolymer. While achieving low emissions as tested by VDA 275 was not a major hurdle, assessing the UV stability of these grades was an issue.

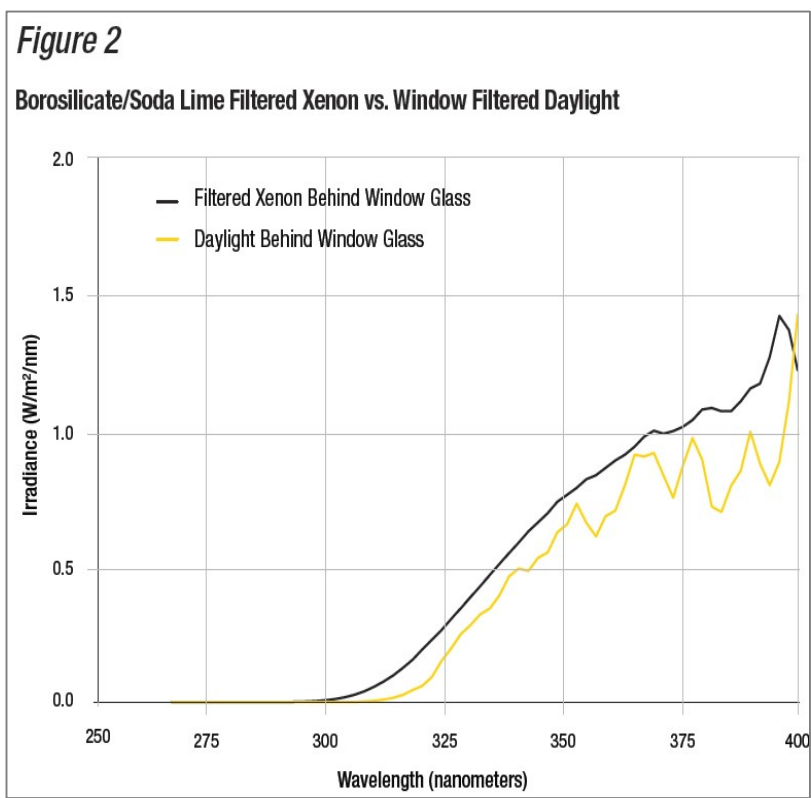
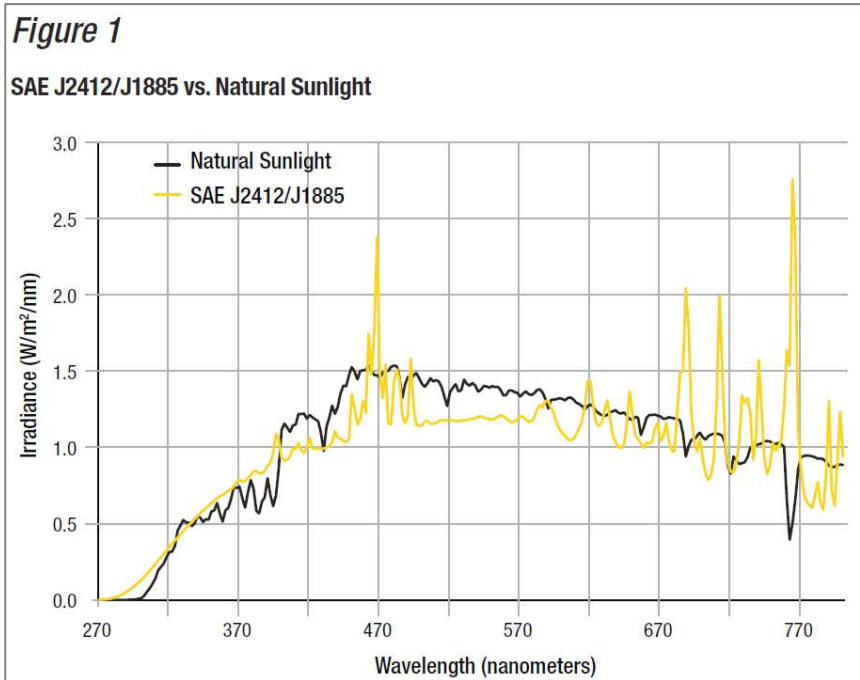
There are many patents covering the formulation of low emission, UV acetal copolymer. A typical formulation would contain UV absorbers, hindered amine light stabilizers, antioxidants, processing aids, formaldehyde scavengers, and other co-stabilizers. VOC reduction as measured by VDA 275 shows conventional UV colors exhibiting emissions in the range of 30 to 50 ppm or higher, as previously reported. Low emission, UV acetal copolymer in conventional colors can exhibit a tenfold reduction, with values typically in the 3 ppm range or less.

The next step of development after achieving low VOC performance was to look at the UV performance of these colors. Testing was conducted using standard xenon arc accelerated method SAE J2412 for 1,240.8 kJ/m² exposure. To our surprise, UV performance was poor using this test method, with significant color change after exposure, and the onset of crazing/ micro-cracking occurring in as little as 200 kJ/m² of exposure. Significant development work ensued to improve the UV performance in SAE J2412 while maintaining good low VOC performance. This was important for the U.S. OEMs that rely on this method, or modifications to this method. We quickly learned that no combination of UV stabilizers and co-stabilizers could optimize performance for both UV and low VOC.

During this time, we did commercialize a low emission UV grade for one of the Asian OEMs on a limited basis, based on their internal testing and approval in Japan. No issues with UV performance were reported. Based on this, a review of accelerated UV test methods was conducted. A summary of that review is presented in Table 4. SAE J2412/ J1885 was the first widely used accelerated xenon method for interior trim. This method was developed in the late 1980's in most part by General Motors and was quickly adopted by Ford and Chrysler. As shown in Table 4, as other OEMs have developed their own xenon methods over the years, the trend has been to use alternate light filtering methods to virtually eliminate wavelengths shorter than 320 nm. In contrast, SAE J2412/J1885 has wavelengths down as low as 270 nm present in the light source. The use of a 320 nm cut-off is supported by the lack of shorter wavelengths in natural sunlight and the use of improved UV automotive glass over the years. Figure

1 shows the spectral power distribution of SAE J2412/J1885 xenon source versus natural sunlight [3]. It does show the higher amount and shorter wavelengths present in the xenon method versus sunlight. Figure 2 shows the spectral power distribution of a xenon lamp with the Borosilicate inner and Soda Lime outer filter configuration versus window filtered daylight. It is obvious from these graphs that the SAE J2412/J1885 does not match the actual sunlight conditions inside the vehicle as well as those methods with the 320 nm cut-off.

Most OEMs rely solely on the accelerated xenon method of their choice to predict long-term performance in the vehicle. General Motors, however, uses a referee method GM 9538P to validate the accelerated xenon results. This referee method is outdoor exposure in Arizona under glass using a solar tracking box to accelerate exposure by following the sun's trajectory throughout the day. Performance in this referee method is the ultimate criteria for UV performance and will override the results of the accelerated xenon testing per SAE J2412/ J1885.



Based on all of this review, it became obvious that we needed to assess the performance of the candidate low emission, UV stabilized acetal copolymer formulation in accelerated xenon testing using the 320 nm cut-off, as well as the GM 9538P referee solar method. Accelerated xenon exposure was conducted using Ford FLTM BO116 -01 and VW PV1303 methods. As expected based on the Asian OEM approval, UV performance for the low emission grade was excellent. Color change (DE*) after exposure was less than 1.0 CIE Lab units with no issue with crazing/micro-crack formation. This quickly explained why the Asian OEM that completed UV testing itself had no issue with the UV stability of the product.

Furthermore, GM referee solar method GM 9538P was conducted on a range of 12 GM colors. SAE J2412/J1885 was also conducted

on this same sample set. Data in Table 5 shows that while the accelerated xenon method predicted failure due to high DE* or poor visual performance, the solar method showed excellent performance. GM engineers were consulted on this finding and they did explain that on rare occasions the accelerated xenon method SAE J2412/J1885 has predicted a false failure after the solar testing results were obtained. They agreed to not require xenon accelerated testing and only rely on GM 9538P data. Chrysler followed suit, with reference to the ASTM G147. Accelerated UV testing is not an issue with other OEMs in all three regions of the world.

Conclusion

Generally, parts suppliers paint or plate plastic parts if the desired color is not achievable, if the color is achievable but has surface defects, if the UV stability is poor, if the gloss is not correct, or if the metallic effect is not achievable. Painting or plating requires one or more secondary processes which require part handling and added cost. Parts that are painted or plated can no longer be reground or recycled and are not considered “green.” It has been shown that engineering resins can be formulated to eliminate the need for painting or plating.

In the case of metallic colors, satin metallic appearances are available and commercial for critical appearance applications such as automotive interior applications. Parts include door handles, trim bezels, speaker grilles, and knobs. The combination of formulation, mold design, and processing makes this possible. Cost savings are in the \$1 to \$4 range per part, which can easily exceed \$1 million in total savings for one application alone. Furthermore, we have shown that UV stabilized molded-in-metallic acetal copolymer formulations can be created that significantly reduce VOCs from the material itself. These options allow the OEM to get “green” by eliminating painting, to save “green” through part cost reduction, and to keep “green” by utilizing low emission acetal copolymer formulations. Additionally, it has been shown that conventional Xenon arc accelerated UV testing SAE J2412 predicts a false failure with low emission, UV stabilized acetal copolymer and should not be used to predict UV performance. xenon methods with a wavelength cut-off of 320 nm or above, or actual solar testing, should be used to assess the UV performance of these grades.

References

- [1] B. Mulholland, "Get Green Without Paint: Molded-in-Metallic Engineering Resins Appearance Applications," Society of Plastics Engineers, Proceedings, ANTEC® 2010
- [2] "JAMA Voluntary Action Program to Reduce VOCs in Passenger Compartment," JAMA Report No. 98, JAIA Translation (year unknown)
- [3] "Sunlight vs. Artificial Light Sources," Brochure, Atlas Material Testing Solutions

Data Tables

Product performance and material data values included in this article are either based on evaluating laboratory test specimens and represent data that fall within the normal range of

properties or were compiled from various published sources. To the best of our knowledge, the information contained in this article is accurate; however, no representation is made as to its suitability in any specific application for establishing maximum, minimum, or ranges of values for specification purposes.

Color data presented in the accompanying tables have been calculated under illuminant "D-65," 10° observer, specular included, expressed in CIE Lab units, unless otherwise noted.

The foregoing represents proof-of-concept data on small-scale replicas and are approximate in nature. Properties of molded parts can be influenced by a wide variety of factors including, but not limited to, material selection, formulations, part design, processing conditions and environmental exposure. Any determination of the suitability of a particular material or composite and part design for any use contemplated by the user is the sole responsibility of the user.

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