MAGNUM™ ABS:
Superior Coloring for ABS Resins

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Authors:
Kenneth Lam – Senior Development Specialist, Trinseo (Hong Kong) Ltd.
Kurt Wong – Senior Development Specialist, Trinseo (Hong Kong) Ltd.

ABSTRACT

Acrylonitrile-butadiene-styrene (ABS) resins are widely used for applications such as appliances, toys, office equipment, sanitary wares, and more. Coloring of ABS resins can typically be achieved by color compounding at a coloring house, or through mixing natural color resins with color masterbatches. Historically, manufacturers of end products using ABS resins, and processors like injection molding workshops, have experienced coloring issues with typical ABS resins produced using the batch emulsion process. These issues include: 1) the base color of the natural resins is inconsistent, with potentially significant lot-to-lot variation in the base color of the same natural resin grade, and 2) different natural ABS resins exhibit varying shades of yellow. When manufacturers of end products receive different lots of ABS resins from the same producer, or different ABS resins from different producers, extra operations are required for color matching, incurring additional resources and costs. For end product manufacturers using natural color ABS resins with color masterbatches, a higher pigment loading is frequently needed to mask the variations in yellow base color from different lots or different grades of ABS resins. Additionally, the thermal stability and light stability of ABS molded parts are primary concerns of end product manufacturers. There is a clear need for improving the coloring efficiency of ABS resins used for various end product applications. This study discusses the light stability and thermal stability of several ABS resins. It is intended to provide information to manufacturers of end product parts to select the optimum ABS materials, especially for parts requiring light colors.

Contents

1. INTRODUCTION

Trinseo is a global materials solutions provider and manufacturer of plastics, latex binders, and synthetic rubber. MAGNUM™ ABS resins by Trinseo are used in a vast selection of products intrinsic to people's daily lives, including appliances, automotive, medical devices, furniture and sanitary products. There are two primary methods for commercial production of ABS: the batch emulsion process, and the mass continuous process. The industry typically labels these as emulsion ABS (eABS) and mass ABS (mABS). MAGNUM™ ABS is produced using the mass continuous process, which has a number of key advantages over the batch emulsion process. This study focuses on the superior advantages of using MAGNUM™ ABS over other ABS resins for products in which coloring is important.

2. COLOR CHARACTERISTICS OF MAGNUM™ ABS

ABS resins are typically produced through two different manufacturing processes: the batch emulsion process, and the mass continuous process (used to produce MAGNUM™ ABS). In the batch emulsion process, butadiene, styrene, acrylonitrile, emulsifier and salt are used to produce grafted rubber concentrate, which is then compounded with styrene acrylonitrile (SAN) resins to produce ABS resins. During this process, not all emulsifiers or salts can be removed; they remain as impurities in the natural emulsion ABS, causing a yellowish base color. The depth of yellow will depend on the levels of impurities in the resins. In the mass continuous process, polybutadiene rubber, styrene and acrylonitrile are used and polymerized into ABS resins. Because emulsifiers and salts are not used in the mass continuous process, the base color of the natural ABS resins is consistently white. Figure 1 is an image comparing the base color of MAGNUM™ ABS produced by the mass continuous process with a typical emulsion ABS produced using the batch emulsion process. The natural MAGNUM™ resins on the left are significantly whiter in color. This simplifies color matching, particularly if light final colors are desired.

Figure 1: Color of granules: MAGNUM™ ABS (on the left) and a typical emulsion ABS (on the right)

2.1 COLOR STABILITY UNDER UV LIGHT

Natural ABS resins without pigments will undergo color change when exposed to ultraviolet (UV) light. The main effect is an increase in yellowness, as indicated by an increase in the b* component (in CIE L*a*b*), due to photo-oxidation of the polybutadiene rubber and styrene acrylonitrile (SAN) components of the ABS. This photo-oxidation will also affect the gloss of the molded parts. Figure 2 illustrates the color change results of two natural ABS resins (MAGNUM™ A136 and eABS1) after a QUV-A weatherability test. As MAGNUM™ A136 carries a much whiter base color than eABS1, its b* value reached the original b* value of the unexposed eABS1 after approximately 48 hours of QUV-A exposure (equivalent to around eight months of outdoor exposure). The actual color shift of the natural color molded plaques can be seen in Figure 3. In addition to color stability in the QUV-A test, gloss retention is a key requirement for ABS resins. Figure 4 indicates that natural color plaques molded from MAGNUM™ A136 retained more gloss than those made from eABS1 after 96 hours of exposure to the QUV-A test.

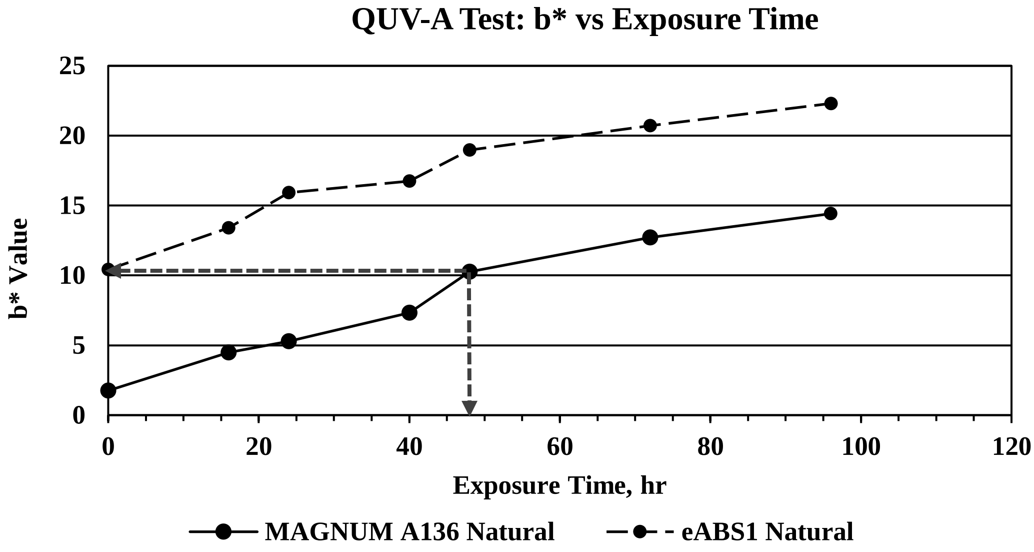


Figure 2: Color shift of natural ABS resins with exposure time in QUV-A test

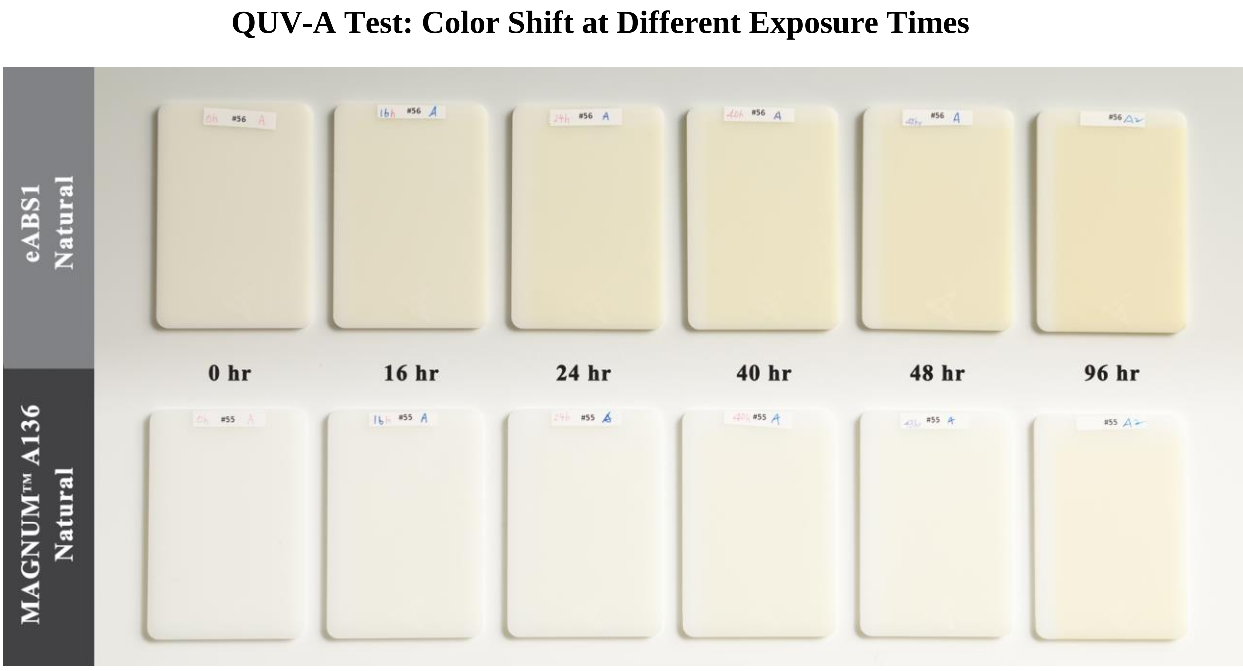


Figure 3: Photographic color shift of natural ABS resins with exposure time in QUV-A test

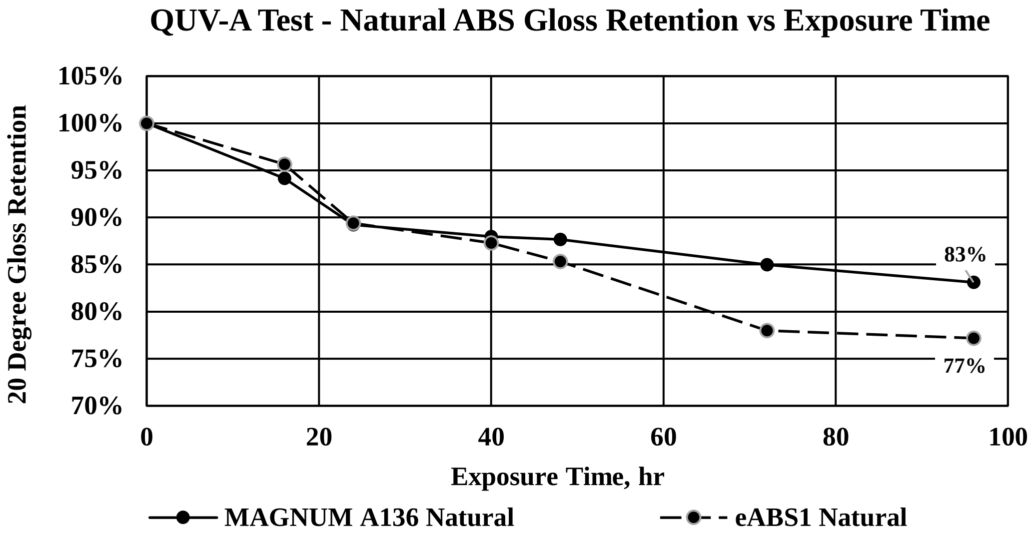


Figure 4: Gloss retention of natural ABS resins with exposure time in QUV-A test

2.2 THERMAL STABILITY OF NATURAL ABS RESINS

Parts or end products made with ABS resins may be stored in elevated temperature environments for extended periods of time (e.g. during long-distance shipment in container vessels). This subjects the products to color change due to thermal degradation. One aging test to simulate elevated temperature storage and transportation is to put the molded plaques in an oven heated to 70 degrees Celsius for four weeks. This oven aging test was conducted on molded plaques of natural color MAGNUM™ A136 and eABS1, with the results shown in Figure 5. These indicate that natural MAGNUM™ A136 has significantly better thermal stability than natural eABS1 after four weeks of exposure, with much lower color shift expressed in delta E* = $[(\text{delta } L^*)^2 + (\text{delta } a^*)^2 + (\text{delta } b^*)^2]^{½}$.

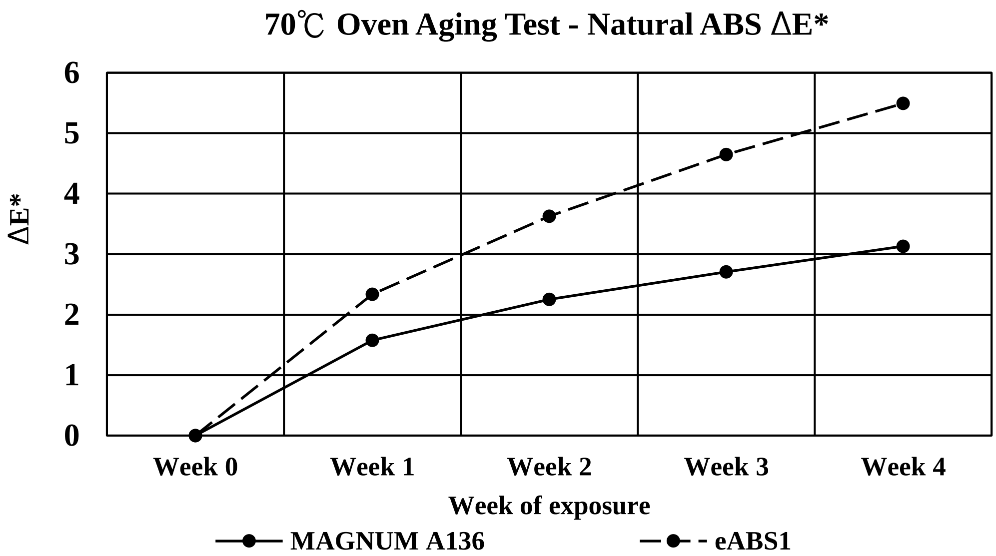


Figure 5: Color shift of natural ABS resins with exposure time in oven aging test

3. IDEAL FOR CHALLENGING COLORS

With a natural white base color, MAGNUM™ ABS is ideal for producing challenging colors such as bright whites or greens. Figure 6 displays color plaques molded from MAGNUM™ A136 and an emulsion ABS, both with 1% loading of a white masterbatch. The MAGNUM™ A136 plaque on the right is markedly whiter.

Figure 6: Color plaques molded from ABS resins with 1% white masterbatch

Figure 7 shows two washing machine door kits. The one on the right is molded using MAGNUM™ A136, and is brighter and greener than the one on the left, which is molded from a typical emulsion ABS.

Figure 7: Washing machine door kits molded from ABS resins with 3% green masterbatch
(MAGNUM™ A136 is seen on the right)

4. REDUCED COLORING COSTS

With a whiter base color, MAGNUM™ ABS can save colorant costs for end product manufacturers wishing to achieve bright and/or light colors. The shades Pure White and Super UV White are used as examples in Table 1. For each color, MAGNUM™ A136 was used to match the color plaque made with an emulsion ABS (eABS1 or eABS2) at a coloring house. Using MAGNUM™ A136 required less pigment than the emulsion ABS resins, with cost savings of around US$40/MT in each case.

Color	Resin	Pigment loading	Resin used to match color	Pigment loading	Colorant cost savings with MAGNUM™ ABS	Color in L*a*b*
Pure White	eABS1	4.8% TiO_2	MAGNUM™ A136	2.4% TiO_2	US$40/MT	L* 95.64 a* 0.195 b* 1.17
Super UV White	eABS2	Unknown (not disclosed by coloring house)	MAGNUM™ A136	Less than eABS2	US$40/MT	L* 93.31 a* -0.99 b* 2.17

Table 1: Pigment loading and cost savings when using MAGNUM™ A136

5. GREATER COLOR STABILITY WITH LESS YELLOWING

The color plaques molded from ABS resins as demonstrated in Table 1 were subjected to light stability tests (QUV-A or QUV-B), with the results illustrated in Figures 8 and 9. The addition of titanium dioxide (TiO_2) to ABS resins provides improvement in light stability upon UV exposure. Predictably, the higher the loading of TiO_2, the greater the light stability upon UV exposure. In the QUV-A test (Figure 8), MAGNUM™ A136 with 2.4% TiO_2 loading had less color change (delta E*) than that of eABS1 with 4.8% TiO_2 loading. With eABS1, it took around 50 hours of exposure to reach a delta E* of 2, while MAGNUM™ A136 took 90 hours of exposure to reach the same delta E* level. This indicates a greater light stability performance from MAGNUM™ A136 over eABS1, even with a lower loading of TiO_2 and approximately US$40/MT less coloring costs. In the QUV-B test (Figure 9), even though the pigment loading was lower, the color change (delta E*) of the MAGNUM™ A136 sample was less than that of eABS2. As one example, it took around 24 hours longer (equivalent to six months of outdoor exposure) for MAGNUM™ A136 to reach a delta E* of 3. If the color change (delta E*) limit for an end product manufacturer is 3 after 96 hours of QUV-B exposure, UV stabilizer has to be added to the two ABS in order to meet the requirement. However, based on the difference in light stability results in Figure 9, it is expected that higher loading of UV stabilizers will be needed for eABS2 (incurring higher raw material costs) than for MAGNUM™ A136.

QUV-A Test - Pure White: ΔE* vs Exposure Time

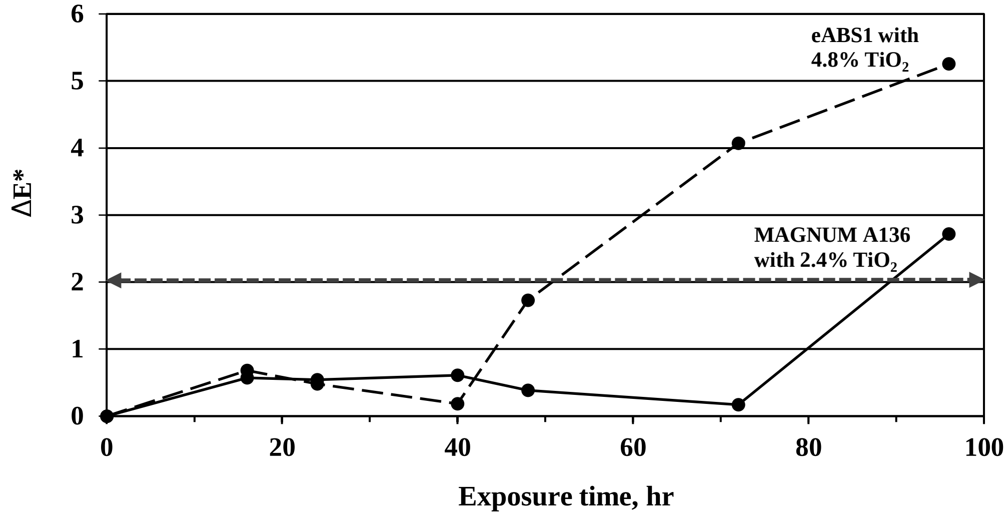


Figure 8: QUV-A test with Pure White color

QUV-B Test - Super UV White: ΔE* vs Exposure Time

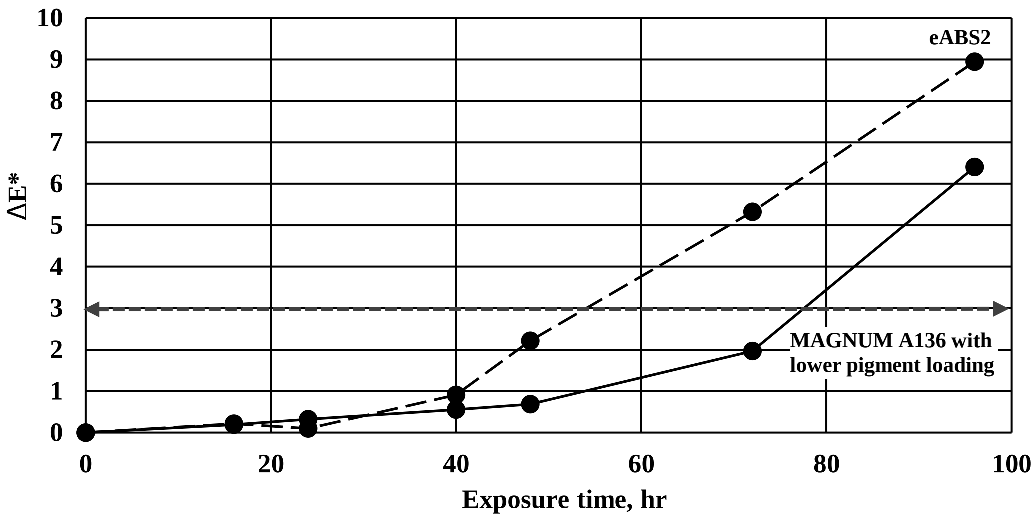
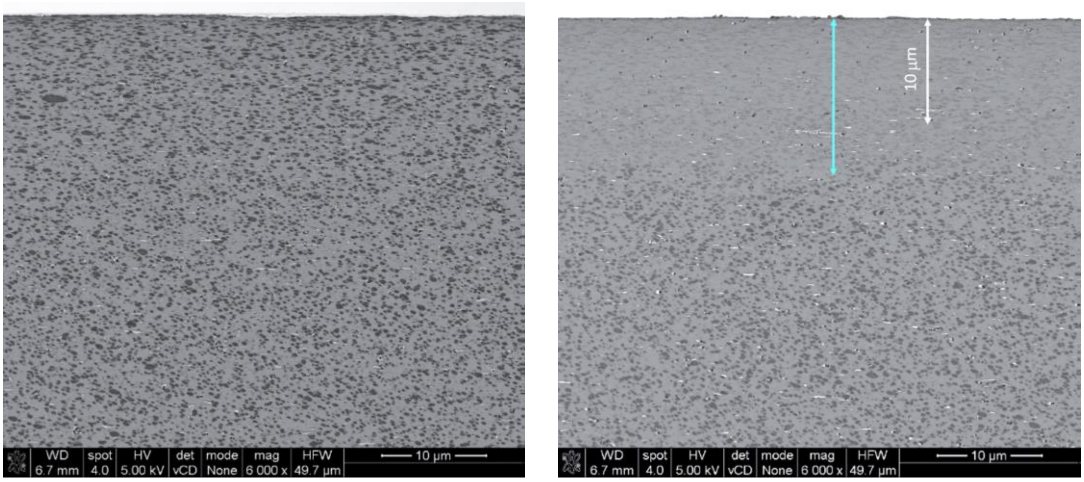


Figure 9: QUV-B test with Super UV White color

6. LONGER LASTING GLOSS

UV radiation attacks ABS resins, affecting both the rubber particles and the SAN matrix. The scanning electron microscopy (SEM) photographs in Figure 10 reveal the effects of UV exposure on the rubber particles. The left photo shows the rubber particles and SAN phase before UV exposure. The dark gray isolated phases are rubber particles and the light gray phase in between is SAN. The right photo shows the effects of UV exposure. The rubber particles are almost invisible over a distance of about 15 microns below the surface. This is because the rubber particles are cross-linked after UV exposure and almost all double covalent bonds in the rubber are lost. In addition, yellow color bodies are formed that cause discoloration or yellowing of the ABS. There was also photodegradation of the SAN phase, which caused further formation of yellow bodies. Chain scission of SAN polymer led to the reduction of the molecular weight of SAN, which can lead to reduced surface gloss.



Not Exposed to UV **Exposed to UV**

Figure 10: SEM photographs depicting photodegradation of ABS resins exposed to UV light

An important requirement of ABS resins in UV light stability tests is how well they retain gloss. The gloss retention of Pure White ABS resins after QUV-A exposure is shown in Figure 11. After 96 hours of QUV-A exposure (equivalent to approximately 16 months of outdoor exposure), the gloss retention of MAGNUM™ A136 (with lower loading of TiO_2) was 10% higher than that of eABS1, clearly demonstrating advanced gloss retention.

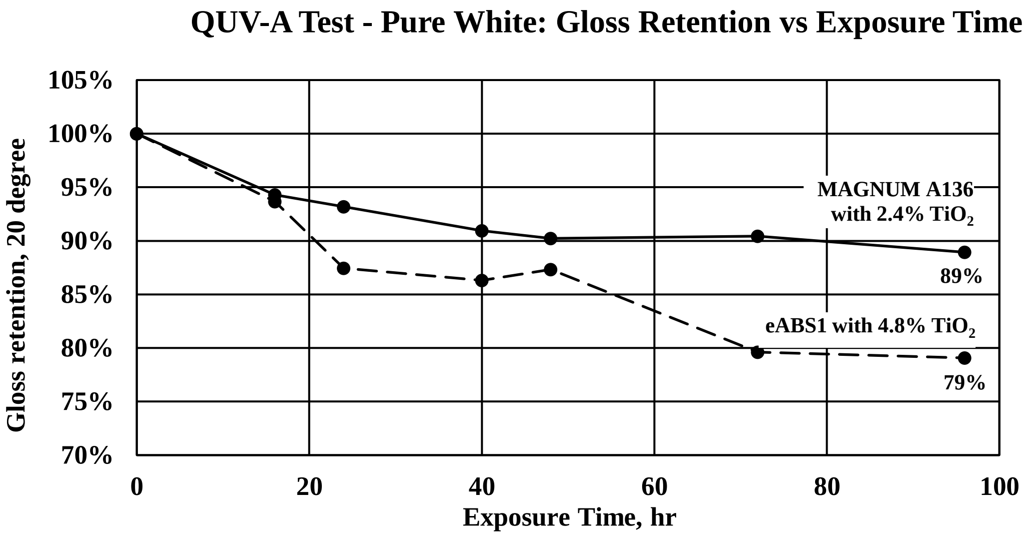


Figure 11: Gloss retention of Pure White ABS resins in QUV-A test

7. GREATER THERMAL STABILITY

To simulate parts or end products stored at elevated temperatures for extended periods of time, Pure White color plaques molded from MAGNUM™ A136 and eABS1 were placed in an oven maintained at 70 degrees Celsius for four weeks. The color shift results are shown in Figure 12. With a much lower color shift expressed in delta E*, MAGNUM™ A136 has significantly more favorable thermal stability than eABS1 after four weeks of exposure. This is consistent with the better color stability at elevated temperature that was reported earlier for the base (unpigmented) MAGNUM™ ABS resin.

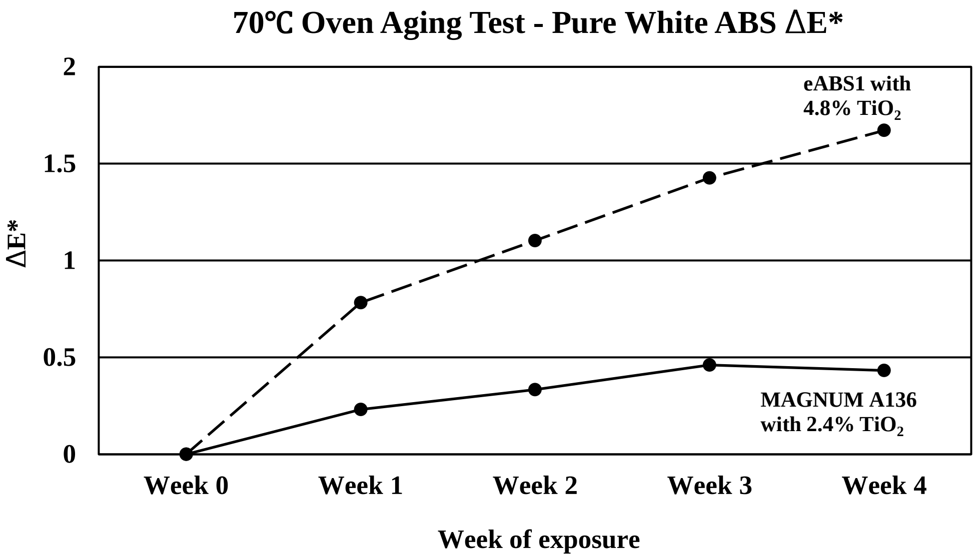


Figure 12: Color shift of Pure White ABS resins with exposure time in oven aging test

8. IMPROVED UV STABILITY AT LOWER COSTS

Manufacturers of end products regularly exposed to sunlight, such as air conditioners and outdoor equipment, will typically have stringent color stability requirements. They may specify the addition of UV stabilizers (UV absorbers or UV blocking additives) into the ABS resins used. A comparison of MAGNUM™ A136, eABS1 and eABS2 in Normal White color, with different loadings of UV absorbers, was conducted to understand the color stability of the three ABS resins. Because TiO_2 improves light stability, only 1.5% of TiO_2 loading was used in each one in order to clearly illustrate the effects of UV absorber amounts on light stability in weathering tests. For each ABS material, two UV absorbers commonly used in the market at equal amounts were included, as well as three total loadings of UV absorbers (0.1%, 0.2% and 0.4%). The natural resins, pigments and UV absorbers were compounded into a Normal White color. Light stability evaluations on the color plaques molded from the resins were conducted with Xenon Arc and QUV-A tests.

Figure 13 illustrates the effects of the loading of UV absorbers on color change of ABS resins across 300 hours of exposure using a Xenon Arc test. For each ABS, the color change (in delta E*) decreased as the amount of UV absorber increased, demonstrating that the UV absorbers used were effective in increasing the light stability of ABS. However, there was a difference in the extent of color change among the three ABS resins tested. To meet a particular color change requirement, e.g. delta E* within 2 at 300 hours of exposure, MAGNUM™ A136 required 0.1% UV absorber, while both eABS1 and eABS2 required 0.4%. Using a higher loading of UV absorbers would incur additional costs for the end product manufacturers – approximately US$20-35 for each extra 0.1% of UV absorber, depending on the UV absorber used. In this example, to meet the delta E* requirement of 2, the cost of UV absorbers for both eABS1 and eABS2 would be about US$60-100/MT higher than that for MAGNUM™ A136.

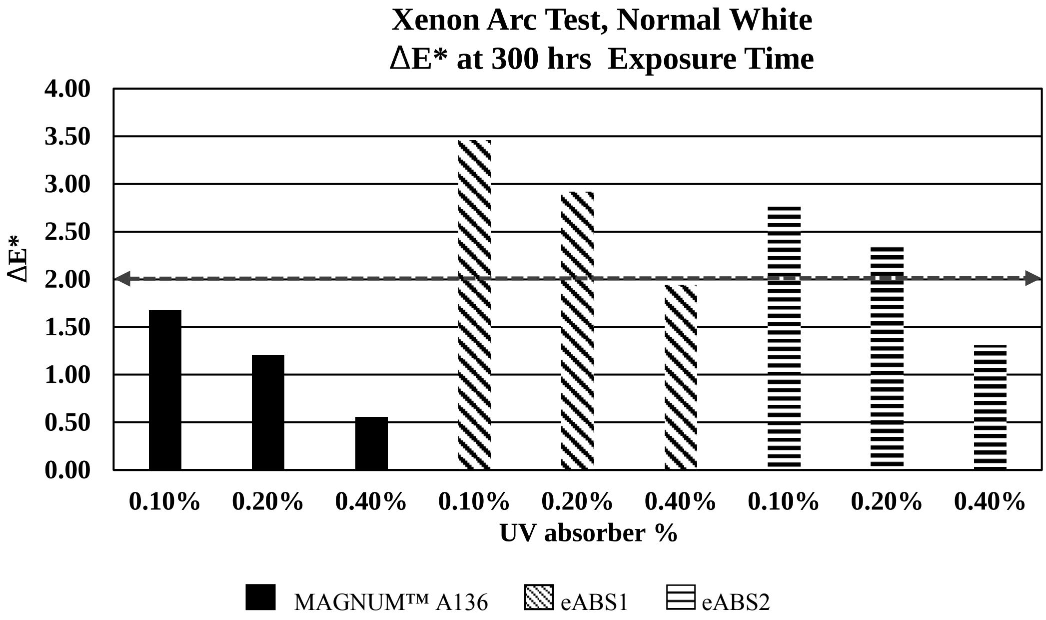


Figure 13: Color shift across 300 hours in a Xenon Arc test;
Normal White ABS resins stabilized with different loadings of UV absorbers

Figure 14 shows the effects of the loading of UV absorbers on color change of ABS resins for 96 hours of exposure using a QUV-A test. To meet a particular color change requirement, e.g. delta E* within 2 at 96 hours of exposure, MAGNUM™ A136 needed 0.4% UV absorber. At the same loading amount of 0.4%, the delta E* of both eABS1 and eABS2 far exceeded the limit, indicating that a much higher loading of UV absorber is necessary to meet the delta E* requirement. Again, this would incur significant costs for the end product manufacturers. Figure 15 is a photo illustrating the actual color shift of the molded plaques in the QUV-A test.

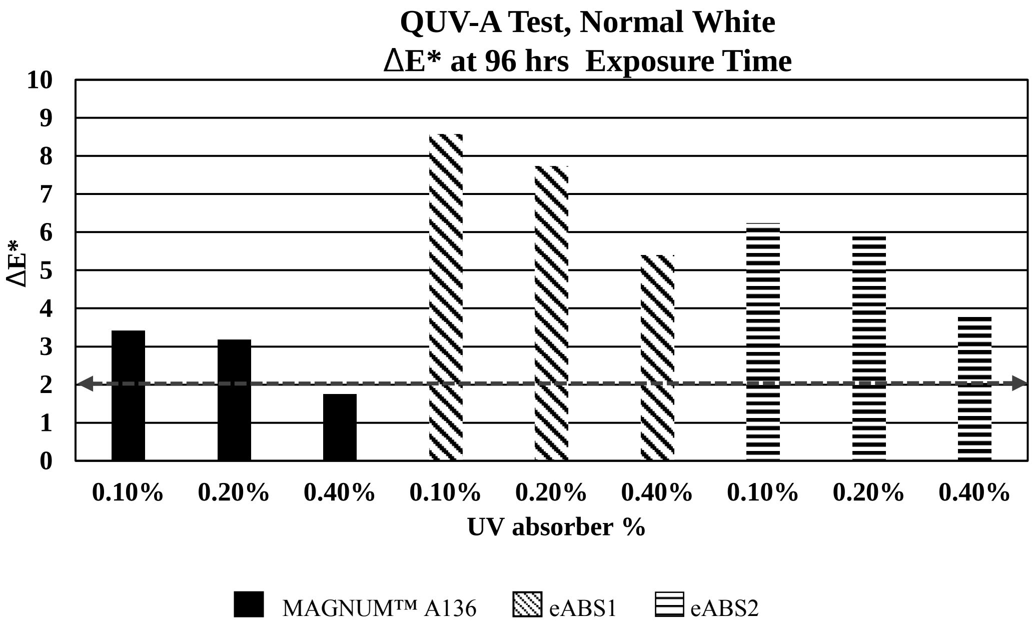


Figure 14: Color shift across 96 hours in a QUV-A test; Normal White ABS molded plaques stabilized with different loadings of UV absorbers

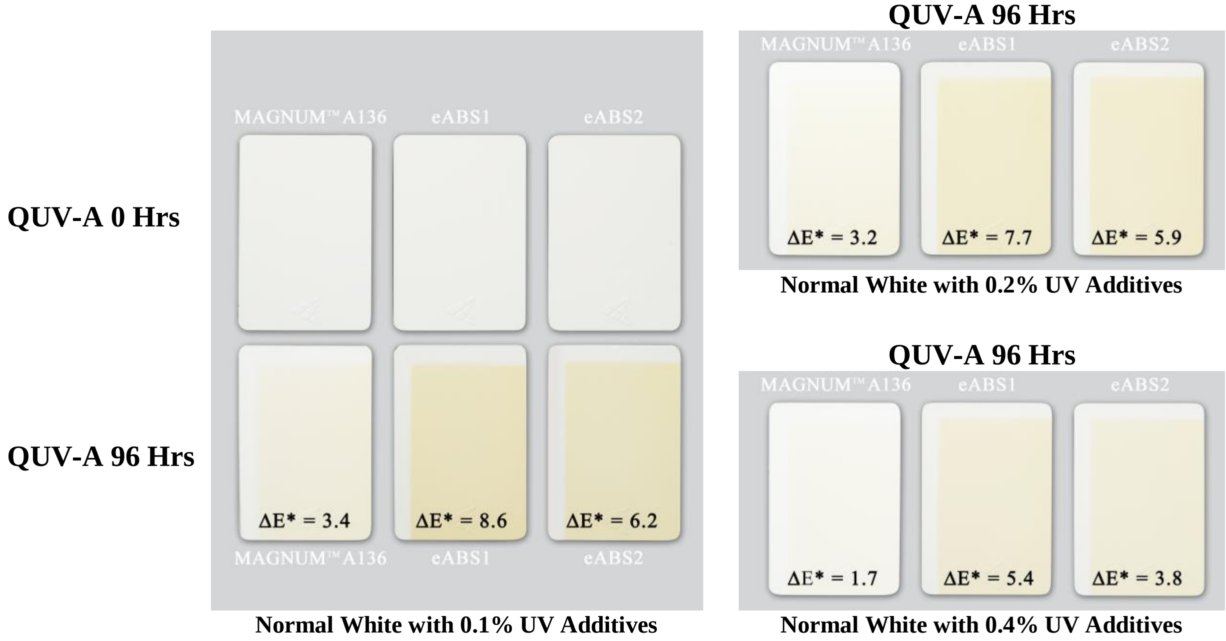


Figure 15: Photographic color shift across 96 hours in a QUV-A test;
Normal White ABS plaques stabilized with different loadings of UV absorbers

Figures 16 and 17 investigate gloss retention with 0.4% UV absorber loading for the molded plaques exposed to the Xenon Arc and QUV-A tests respectively. The figures demonstrate that MAGNUM™ A136 has preferable gloss retention performance to the other two emulsion ABS resins.

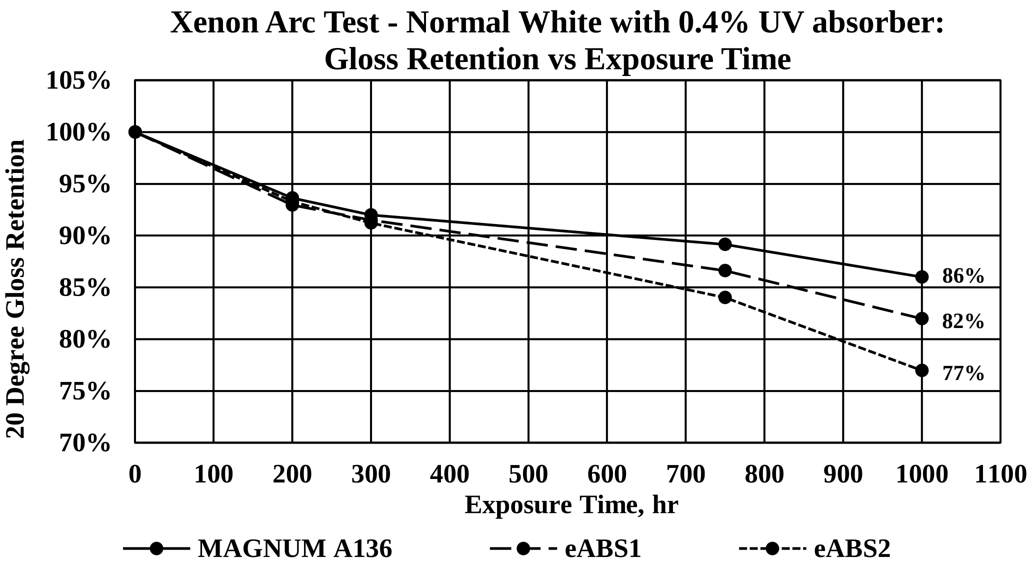


Figure 16: Gloss retention of Normal White color ABS resins with 0.4% UV absorber in Xenon Arc test

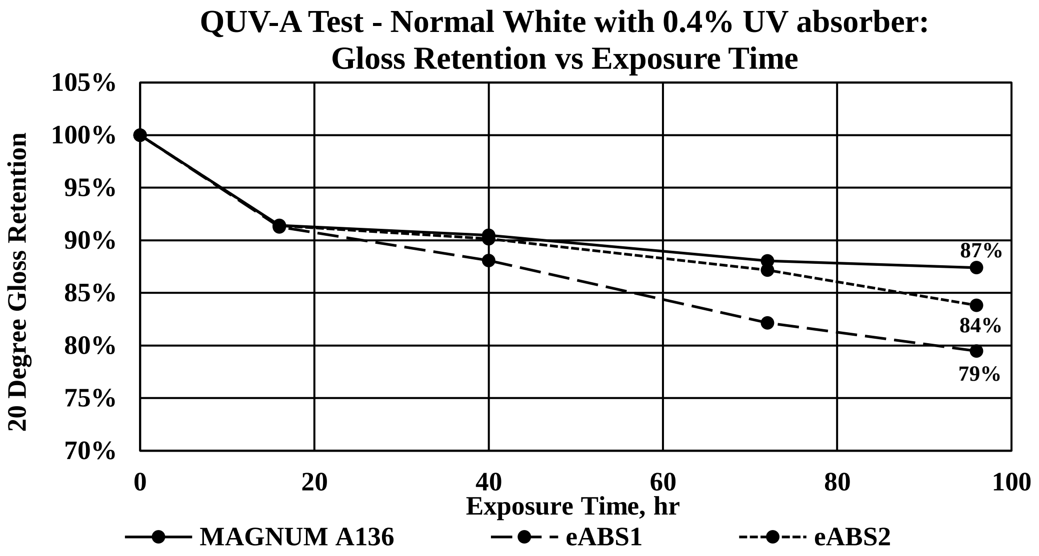


Figure 17: Gloss retention of Normal White color ABS resins with 0.4% UV absorber in QUV-A test

9. CONCLUSION

The results of this study clearly show that MAGNUM™ ABS produced by the mass continuous process has the following advantages over emulsion ABS resins produced using the batch emulsion process:

- The white base color of MAGNUM™ ABS helps to accomplish challenging colors, e.g. whiter and brighter shades.
- Cost savings are evident in colorants for light colors when using MAGNUM™ ABS.
- Even with a reduced pigment loading, MAGNUM™ ABS offers better color stability and gloss retention through weatherability for both natural and white colors.
- With MAGNUM™ ABS, superior thermal stability is proven for both natural and white colors, with reduced pigment loading.
- Significant UV stabilizer cost savings will be made for applications requiring excellent color stability when using MAGNUM™ ABS.

MAGNUM™ ABS offers significant benefits over emulsion ABS, especially when seeking optimum color performance and stability. The whiter base color of MAGNUM™ ABS makes it substantially more cost-effective for producing whiter, brighter shades, with markedly less yellowing. This color stability continues after UV exposure, plus costs of UV stabilizers reduced while preserving gloss. MAGNUM™ ABS can also withstand elevated temperature environments for extended time periods, increasing efficacy during storage and transportation. In practical terms, choosing MAGNUM™ ABS over emulsion ABS can deliver consistent color and superior aesthetics to customers, with outstanding product efficiency and cost savings.

END

For enquiries, please contact

Ms Phyllis Fong

phyllisfong@trinseo.com

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