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Developments in Low HAP Gel Coat Technology

ABSTRACT

Many of the original low HAP (hazardous air pollutant) gel coats formulated to meet the future U.S. EPA MACT standards use existing polyester resin technologies to achieve the reduced styrene monomer and methyl methacrylate levels. These products tend to be inferior to conventional products in process characteristics, water resistance and physical properties. These shortcomings have left the marine, transportation and cast polymer industries with uncertain futures in maintaining the quality of their products. An extensive product development program designed to improve these undesirable characteristics will be demonstrated.

This paper will explore the parameters used to develop these next generation low HAP gel coat products. It will illustrate the improvements in water resistance and physical properties along with the improved weathering characteristics of these new coatings. The handling characteristics of these new products will also be reviewed.

INTRODUCTION

Initial low HAP gel coats were developed and formulated in one of several ways.

- Existing gel coat resins were formulated into coatings with lower monomer levels and higher filler levels.
- Alternate non-HAP monomers or solvents were used to replace styrene and methyl methacrylate.
- Existing low viscosity polymers were used to develop coatings with low HAP levels.

Using existing gel coat base resins to formulate low HAP products produced gel coats with acceptable physical properties and weathering characteristics but created numerous process related problems. In order to maintain equivalent sag control to conventional gel coats, the low shear viscosity of the low HAP product needed to remain the same. This resulted in significantly higher high shear viscosities. These high viscosities made the gel coats much more difficult to pump and atomize during the spray application. These difficulties sometimes led to surface defects and other problems.

The replacement of styrene and methyl methacrylate with alternate monomers was impractical for several reasons. These alternate monomers did not reduce viscosity as effectively as styrene, were sometimes quite costly and typically exhibited poor cure when applied in a thin film. The use of non-HAP solvents to replace styrene generated products with acceptable process characteristics but sometimes exhibited other problems such a poor weathering or water resistance. The technique of developing low HAP gel coats with existing low viscosity resin bases was the approach taken by most of the industry. These products eliminated many of the processing problems encountered with using conventional gel coat base resins and were generally more cost effective than using alternate monomers. The problem with these products is that they tended to be inferior to conventional products in physical properties, water resistance, and UV resistance. These products would tend to have lower HDT temperatures, which led to an increase in surface profile problems for the composites industry and potentially more thermal cycle test failures for the cast polymer industry. They typically showed lower water resistance, which could potentially lead to an increase in blistering problems for the marine industry. In some cases, they exhibited more yellowing and lower gloss retention than conventional products under exposure to UV radiation.

These deficiencies demonstrated the need for a further enhancement of low HAP coatings technology. A program was initiated to develop new polymers for use in low HAP gel coat products. These new polymers would need to address the issues of inferior physical properties and water resistance while maintaining the ability to formulate gel coat products with excellent processing characteristics.

DEVELOPMENT

A Fitness for Use program was initiated where development parameters were put into place for the creation of a new polymer for low HAP gel coat manufacture. This new polymer was to be developed with the following characteristics.

- Physical properties similar to those of a conventional Iso NPG base resin used in the manufacture of gel coats.
- A polymer viscosity that enables producing a low HAP gel coat with acceptable processing characteristics
- High polymer reactivity that enables a coating to be formulated with excellent thin film cure.
- Polymer chemistry that generates equivalent or better water/UV resistance than conventional gel coats.

Once these parameters had been determined, a polymer synthesis program was undertaken where several potential chemistries were to be investigated. Potential candidates were synthesized and those that successfully met the physical property criteria were formulated into coatings. These potential polymer candidates were formulated into low HAP marble clear and white pigmented coatings, which were subjected to a standard array of initial tests to determine their viability as a product. Examples of this initial testing were rheology and cure standards that indicated whether the coatings would meet general processing requirements such as acceptable spray characteristics, sag control and thin film cure.

Remaining polymer/coating candidates were then used in the construction of test panels for durability testing. The products were evaluated for water resistance in a 1000 hour 150°F water soak test with results being compared to a conventional Iso NPG and standard low HAP gel coat. Accelerated weather testing was also performed on these panels using UVA-340 lamps for 1000 hours. Color change and gloss retention were measured at 250 hour intervals and results compared between the candidates. Thermal cycle testing would be run on the new low HAP clear product and water/weather resistance would be revivified on the pigmented systems.

Results from this testing would lead to further optimization and synthesis of the new polymer until the final polymer formulation was selected. Once selected, a scale-up program was initiated where the process characteristics of the coatings were determined on a larger scale by using the materials in production at various test sites. Thermal cycle testing would be run on the new low HAP clear product and water/weather resistance would be revivified on the pigmented systems.

RESULTS

The low HAP polymer/coating development program yielded a new innovative line of products that met virtually all parameters set in the initial Fitness for Use criteria. Figure 1 compares the physical property measurements of the new base polymer versus a conventional Iso NPG gel coat base polymer. Results were obtained on polymer samples with styrene levels as formulated in the coating. Thus, the Iso NPG had a styrene level of 50% and the low HAP product was at 40%. The lower styrene levels in the low HAP products help explain the lower HDT levels. The HDT of the new polymer as compared to the first generation low HAP products shows an increase of approximately 15-20 DF and should translate to an improvement in surface profiles and resistance to print/distortion in the composite coating The higher tensile elongation along with fairly equivalent flexural and tensile properties to the Iso NPG assures a product with excellent strength and resistance to cracking.

The 150°F water exposure test results are shown in Figure 2. The new low HAP coating shows considerable resistance to blister formation over the initial low HAP product. The new low HAP product shows equivalent, if not better results than the conventional ISO NPG product, which should make it ideal for use in water exposure conditions. Testing was performed several times with initial lab synthesized and production scale batches. All testing showed similar water resistance characteristics.

The accelerated weather test results show the new low HAP coating to have a significant improvement in resistance to yellowing over the conventional Iso NPG and initial low HAP products.

The gloss retention of the new low HAP coating is significantly improved over the initial low HAP coating and is equivalent to the conventional Iso NPG. The results of this test are shown in Figure 3 with graphical representations of the overall color change and gloss retention in Figures 4 and 5, respectively.

The processing characteristics of these new products were evaluated by making parts in a standard production environment. The low HAP clear spray and cure characteristics were typical of standard conventional products and exhibited easy demold and good color. Subsequent thermal cycle testing of units produced during this test showed comparable results to parts produced with a conventional Iso NPG product. The new pigmented low HAP product was also field tested at various sites and showed superior handling characteristics over existing low HAP coatings. Figure 6 shows viscosity comparisons between conventional, existing low HAP, and the new low HAP product. Equivalent low shear (2 RPM) viscosity results indicate the products would have similar resistance to sag. However, the different high shear (20 RPM) results point to differences in how easily the materials are pumped and atomized. The lower the viscosity, the easier the material is to handle. The results show a distinct improvement in the new low HAP product over existing low HAP technology.

CONCLUSIONS

This newly developed line of low HAP products has shown marked improvement in water resistance and resistance to yellowing over existing low HAP technology. These products approach the same physical properties and handling characteristics of conventional products. This new technology will continue to be further developed and will lead to new, innovative coatings that continue to reduce HAP content, improve weathering characteristics and give the composites industry a product they can confidently use to build quality parts and still meet environmental and workplace exposure regulations.

Figure 1.

		ASTM	Conventional Iso NPG	New Low HAP
Flexural Strength	Psi	D-790	19,481	16,180
Flexural Modu-	x10^6psi	D-790	0.53	0.57
Tensile Strength	Psi	D-638	11,813	10,482
Tensile Modulus	x10^6psi	D-638	0.53	0.46
Elongation	%	D-638	3.3	4.1
Heat Distortion	°C/°F	D-648	93/199	83/181
Barcol	934-1	D-2583	43	48
Resin catalyzed with 1.0% MEKP-9. Ultimately post-cured for 5 hours @ 100°C.				

Figure 2.

	Hours	Blisters	Color	Fibers	Cracks	Gloss
Next Generation Low HAP	250	0	0	0.5	0	0
	500	0	0	0.5	0	0
	750	0	0	0.7	0	0
	1000	0	0.3	0	0	1
Conventional Iso NPG	250	0	0	1	0	0
	500	0.3	0	1	0	0
	750	0.3	0	1	0	0
	1000	0.3	1	1	0	1
Initial Low HAP	250	0	0.5	0	0	2
	500	1	0.5	0	0	3
	750	4	1	0	0	3
Rating: 0-No Change ; 5-Fail						

Figure 3.

GEL COAT		**GLOSS**	**DL**	**Da**	**Db**	**DE**
Conventional	initial	92.8				
	250	88.5	-0.23	0.27	1.61	1.65
	500	90.9	-0.44	0	3.42	3.45
	750	88.1	-0.71	-0.09	4.61	4.67
	1000	86.7	-0.72	-0.24	5.91	5.96
Initial Low HAP	initial	93.5				
	250	87.8	-0.59	-0.09	2.23	2.31
	500	89.3	-1.13	-0.33	4.37	4.53
	750	76.6	-1.56	-0.36	5.54	5.77
	1000	50.2	-1.77	-0.29	6.05	6.31
Next Generation Low HAP	initial	92.4				
	250	88.1	-0.04	0.34	0.78	0.85
	500	87.4	-0.16	0.29	1.27	1.32
	750	88.8	-0.18	0.19	2.11	2.13
	1000	85.5	-0.36	0.17	2.26	2.29

Figure 4.

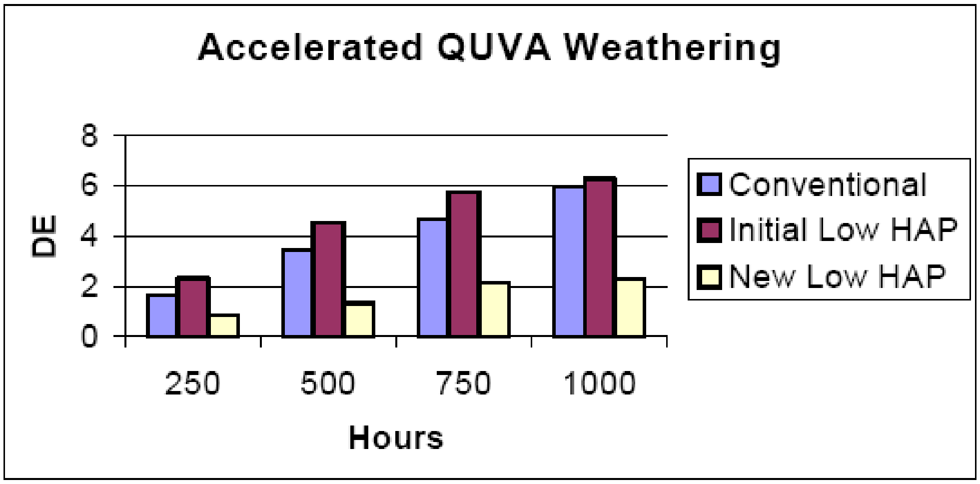

Figure 5.

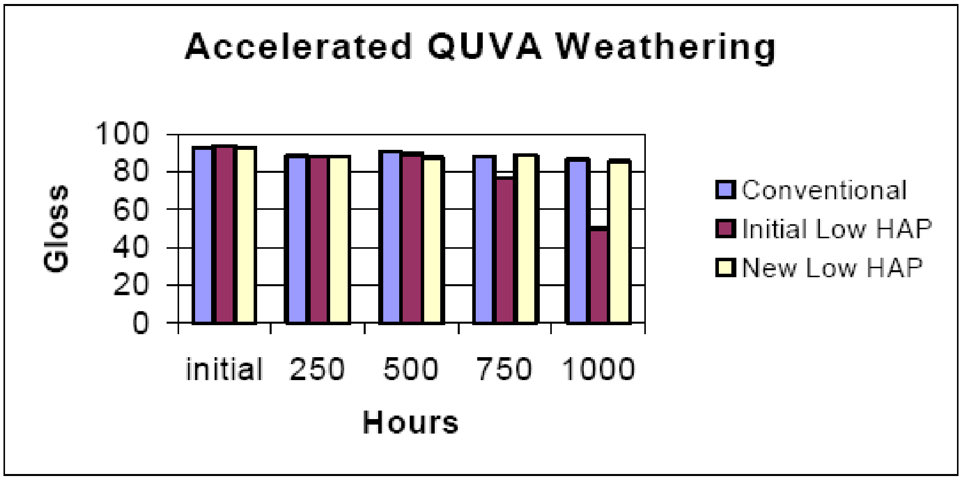

Figure 6.

	Conventional Iso NPG	Initial Low HAP	Next Generation Low HAP
Viscosity RVF, SP #4 @ 2 rpm	36,000	35,000	35,000
Viscosity RVF, SP #4 @ 20 rpm	5,000	6,100	5,650
Thix Index @ 2/20 rpm	7.2	5.7	6.2