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The Development of a Marble Clear Gel Coat with Improved Performance Properties

by

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Abstract

This paper describes the development and optimization of a clear gel coat with improved performance in thermal cycle testing, color, and cure characteristics. The entire process will be outlined beginning with the development of a new polyester resin as the backbone of the new clear and ending with an illustration of the final performance and processing characteristics of the new technology.

Introduction

The clear gel coat is an essential component in the construction of cultured marble products. It must provide the needed durability for years of use by the consumer, yet it must not make a visible color contribution. The lack of color contribution is important so that the beauty of the matrix substrate can remain vibrant and colorful. For the cultured marble manufacturer, the clear gel coat must process effectively in their facility. The clear should give acceptable spray characteristics, sag control, air release, and leveling. It should also provide cure characteristics that allows short manufacturing cycle times for high volume production.

Many of the initial clears gel coat formulated to meet the Composites MACT standard were found to be deficient in several key aspects. Though they met the requirement of having HAP levels under 44%, the various products would tend to be difficult to process under normal manufacturing conditions. They would also show some inferior performance characteristics as compared to conventional clear gel coats with higher HAP contents. Examples of some of the process-related deficiencies were difficulties in achieving fast cure cycles without excessive surface tackiness and difficulties in achieving good spray characteristics. Inferior performance characteristics were typically seen with a higher degree of color contribution, a lower degree of clarity and a drop-off in thermal cycle test results. ANSI Z124.3 requirements for cultured marble lavatories specify that the part shall surpass 500 cycles in thermal shock testing without failure. It was found that many of these initial marble clears could pass the requirement, but barely. Failures at 600-800 cycles were typical while the conventional marble clear products with higher HAP contents would typically surpass 1000 cycles in testing.

With the correction of these deficiencies in mind, a development project was initiated. Early on in the development, it was recognized that in order to eliminate many of the shortcomings in the initial clear gel coats, a new polymer would need to be at the forefront of the development. With this new technology, the formulating of a new clear gel coat could be optimized to achieve the necessary process and performance characteristics.

Development Process

There were four specific goals in the development of the new clear gel coat technology for the cast polymer industry:

- Improve the cure of the product such that manufacturing cycle times can be decreased
- Reduce the surface tack on the back side of the clear
- Improve thermal cycle test results
- Improve the color and clarity of the clear

These goals needed to be achieved while maintaining the ability to formulate products with low HAP content. The cost structure of the new technology could not be significantly higher than what was typically available on the market.

Once these goals had been determined, a polymer synthesis program was undertaken where several potential chemistries were to be investigated. Minimum base resin mechanical properties were specified along with a maximum APHA color of 40. Potential candidates were synthesized and those that successfully met the physical property and color criteria were formulated into a standard clear gel coat formulation with a nominal HAP content of 42%. An array of tests was performed on these formulated products including tests for cure and color which were two of the primary development goals. Other examples of this initial testing were rheology standards that indicated whether the coatings would meet general processing requirements such as acceptable spray characteristics, sag control and air release.

For any of the base resin candidates that met the cure and color goal, the next step in the process was the manufacture of a typical bathroom lavatory using a standardized construction methodology. The construction of the lavatory would also further allow the evaluation of the candidates spray and cure characteristics. The manufactured lavatory was then tested on a thermal cycle tester in accordance with the ANSI Z124.3 test parameters.

The entire process was optimized and repeated numerous times until a base resin was developed that allowed the primary goals to be met. The final step in the development process was the optimization of the clear gel coat formulation itself to give the best overall process and performance characteristics.

Experimental

The base resin synthesis program consisted in maintaining an isophthalic base to the acid side of the polymer. The variants tested were changes to the glycol side of the polymer formulation where the type and amount of glycol was altered. The changes were made with the idea that improvements could be realized in thermal cycle test results by an improvement in mechanical properties of the resin. It was also theorized that these changes would generate a better cure with a reduction in air inhibition characteristics. This would give less surface tackiness on the back side of the gel coat film. Different methodologies of synthesis were also investigated for their effect on polymer properties and initial color. Once produced, the new resins were tested for mechanical properties and needed to meet the minimum test results as shown in Figure 1. Resin candidates that met the minimum criteria were formulated into a clear gel coat using the generic formulation illustrated in Figure 2.

The clear gel coats were tested for wet properties including viscosity, thixotropic index, color, and cure-related properties. Figure 3 shows the cure property comparisons of the various candidates that had met the previous development parameters. R4, R8 and R10 were of particular interest due to their fast cure and low degree of surface tack. These candidates also showed acceptable rheological properties and initial color characteristics.

Cultured marble lavatory tops were produced from these candidates using airless, air-assist spray equipment. The tool shown in Figure 4 was used to produce the parts. During the application of the clear, the material was evaluated for ease of spray, sag control, air release, defect formation, and cure. The gel coat was applied from 18-22 mils wet using a standard MEKP initiator at 1.8%. The gel coat was allowed to cure and a standardized matrix was poured behind it. A general purpose casting resin was used at a calcium carbonate filler loading of 75%. Titanium dioxide was used at a 1% loading and the system was initiated at 1.5% MEKP based on resin weight. The parts were de-molded after cure and allowed to post-cure for a minimum of two weeks prior to thermal cycle testing.

Thermal cycle testing in accordance with ANSI Z124.3 was performed on these lavatory test bowls using the apparatus shown in Figure 5. The basic principle in the test is cycling hot and color water over the same portion of the bowl area. A periodic visual inspection of the bowl is done to look for any cracking in the gel coat or matrix. The ANSI Z124.3 requirement stipulates that the units need to cycle 500 times without defect.

Results

The R4, R8 and R10 based clear gel coats tested on the thermal cycle tester all exhibited good results with gel coat failure taking place after 1000 cycles. Based on the overall positive results of cure, color, and thermal cycle testing, it was decided to further pursue the new polymer technology of R4. Additional lab and production scale-up of the chemistry was undertaken with continued repetition of making lavatory tops and repeated thermal cycle testing. Figure 6 illustrates the average number of cycles to failure of the newly developed technology as compared to the initial generation of the low HAP clear gel coats.

The improvement in thermal cycle test results was realized by two important factors. The first factor was the change to the glycol side of the new resin technology which yielded an improved toughness to the formulated clear. The second factor was the improvement in cure. The improved cure allowed an optimized promoter system in the clear gel coat formulation. This system allowed the development of optimal mechanical properties without short chaining or plasticizing the cured polymer network.

Optimization of the clear gel coat formulation yielded a product with virtually no air inhibition that results in surface tackiness on the back side of the coating. This allowed a substantial reduction in cure times with the ability to pour matrix behind the gel coat brought down to 30 minutes at a 77 °F ambient temperature. The improvement in color between the initial low HAP products and the new technology is illustrated in Figures 7 and 8. The new technology has a lower L value which means it is lighter in appearance over the white substrate than the initial low HAP products. Visually this correlates to a sharper image of the substrate with better clarity. The new technology also has a significantly lower b* value which correlates to an appearance that is much less yellow. These improvements in color and clarity were realized through the low initial color from the new polymer along with the optimization of the formulated clear promoter system.

Conclusion

This development program has demonstrated the technology to formulate a new generation of clear gel coats capable of meeting the Composites MACT standard. Several improvements have been made over initial technologies where significant gains in product durability can be obtained via improved thermal cycle test results. Additional improvements include the color and appearance of the clear as well as improvements in process characteristics with the ability to shorten manufacturing part cycle times via faster cure.

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Figure 1

Minimum Cast Mechanical Properties

Test	Units	ASTM	
Flexural Strength	Psi	D-790	12000
Flexural Modulus	Mpsi	D-790	300
Tensile Strength	Psi	D-638	8000
Tensile Modulus	Mpsi	D-638	300
Elongation	(%)	D-638	3.5
Heat Distortion	(^{o}C)	D-648	70
Izod Impact	Ft.-lbs/in	D-4812	1.5
Barcol Hardness	(934-1)	D-2583	35

Figure 2

Standard Marble Clear Formulation

Ingredient	**%**
Base Resin (70% solids)	**79.50**
Air Release Additive	**0.30**
Fumed Silica	**1.60**
Cobalt 12%	**0.05**
Secondary Promoters	**0.10**
Inhibitors	**0.05**
Thixotropic Synergist	**0.20**
Styrene Monomer	**18.20**
Total:	**100.00**

Figure 3

Cure Data

Base	Gel Time (min)	Peak Exo-therm (°C)	Gel To Peak (min)	Thin Film Gel (min)	Pour Up Time (min)	Tack Free (min)	General Comments
R1	2.5	210.2	5.2	15	25	50	Surface tack remains
R2	2.6	210.9	5.6	20	35	60	Surface tack remains
R3	2.4	220.4	4.8	10	22	50	Surface tack remains
R4	8.0	219.0	7.3	22	35	55	Tack free
R5	18.0	204.1	9.0	24	45	70	Surface tack remains
R6	6.3	211.0	7.6	20	40	65	Surface tack remains
R7	9.9	210.4	8.0	10	25	50	Surface tack remains
R8	6.1	212.0	8.0	12	25	40	Tack free
R9	9.9	211.3	7.3	22	80	120	Tack free
R10	8.0	204.8	9.6	20	35	55	Tack free
R11	14.8	200.1	9.9	35	55	120	Tack free
R12	8.2	215.1	6.9	20	60	120	Surface tack remains
R13	10.5	210.0	8.3	25	60	180	Surface tack remains
R14	23.2	197.9	15.0	50	90	120	Surface tack remains

Figure 4

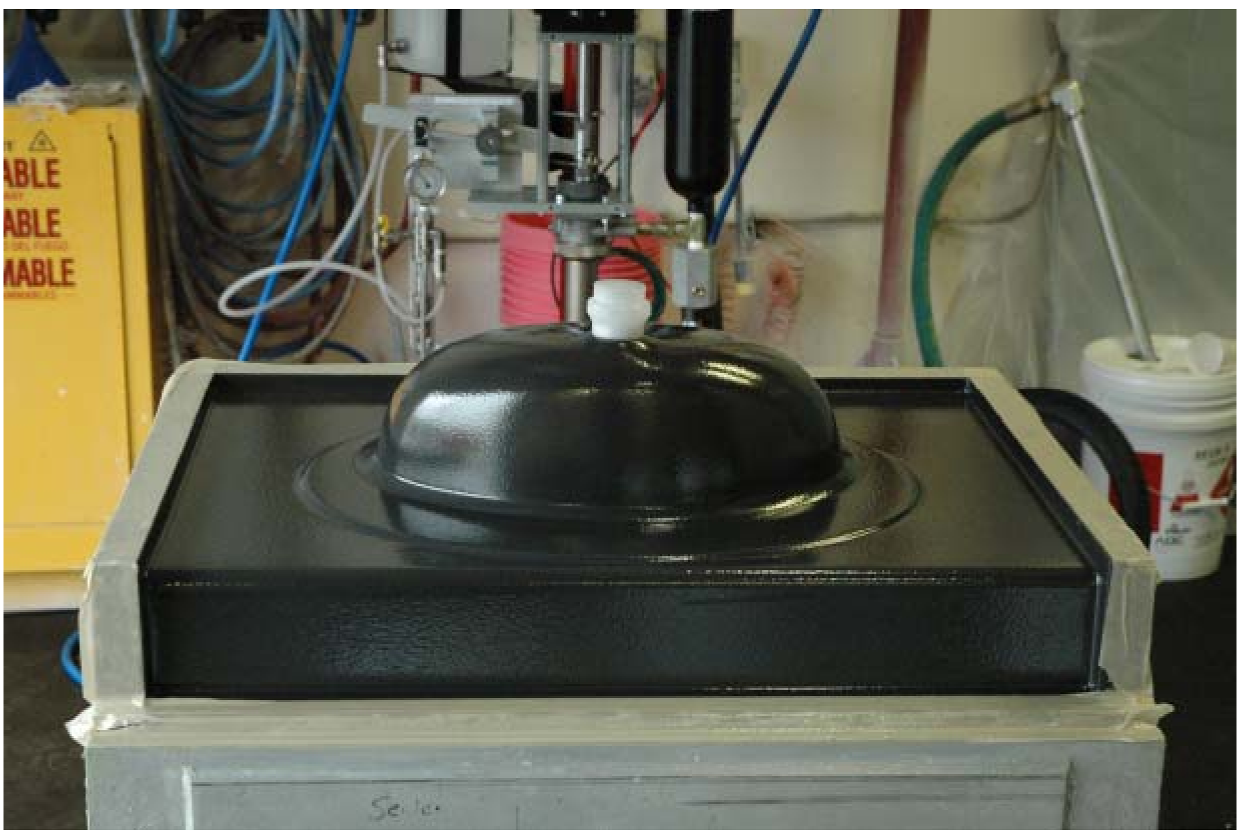

Figure 5

Figure 6

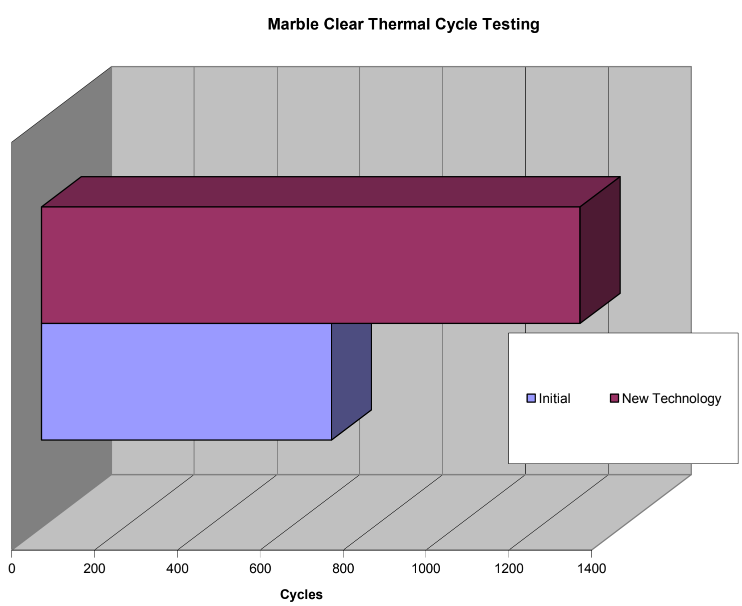

Figure 7

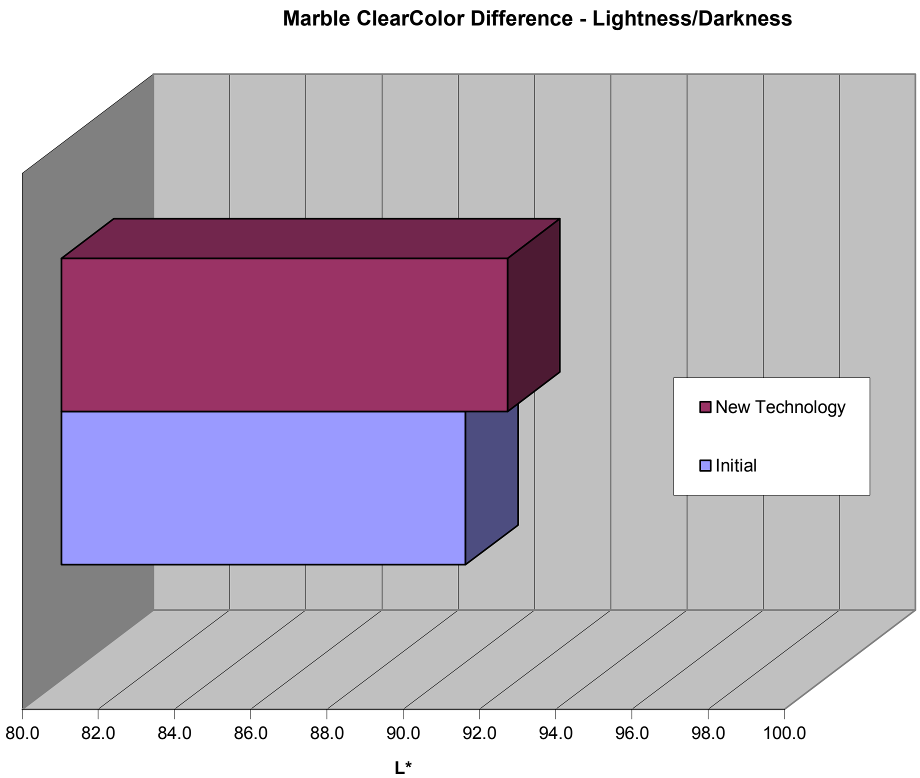

Figure 8