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Development of Blush Resistant Gelcoat

by

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Development of Blush resistant Gelcoat for Marine Application

Boat builders have been restricted to white or pastel boats for underwater application due to the blushing of dark colored gelcoat. Blushing of the dark colored gelcoat is due to the absorption of moisture by the resin, extender pigments and pigments used in conventional gelcoat. The choice of deck colors has not been restricted, as they are not exposed to water. However, a dark colored gel coat used for above water application has a tendency to blush when the boat is shrink-wrapped for storage and transportation. This is due to the condensation of moisture trapped between the shrink-wrap and the gelcoat. Hence, there was a need to develop a gelcoat, which does not blush in color or exposure to water.

A low VOC gelcoat has been developed using a combination of resins and pigments, which has resistance to blushing on exposure to water. The gelcoat panels, when exposed to 185ºF water for 200hrs, give a color change of less than 0.5 ΔE compared to up to 9.0 ΔE with conventional gel coat. Using the newly developed gel coat it will now be possible to make colored hulls without bottom paint that will retain a blush resistance of less than 0.5ΔE.

Introduction

Gelcoats used in the marine industry has to meet stringent performance application requirement. Excellent weather and blister resistant must be met as well as a good spray pattern that results in a porosity free film. The gelcoat must also have easy sanding and buff back properties. Advances in unsaturated polyester resin and gelcoat technology have led to gelcoat manufacturers supplying MACT compliant gelcoat having equivalent weather and blister resistance properties as conventional gelcoat. Gelcoat formulators have developed weather resistant gelcoat using an aliphatic polymer backbone, aliphatic monomers and UV inhibitors. Blister resistance properties have been vastly improved in the past few years by using resins with excellent water resistance characteristics. The blister properties can also be improved by using a vinyl ester barrier coat behind the gelcoat.

However until now, no dark colored gelcoats have been commercially available that can provide blush resistance and meet customer application requirements. Also, dark colored gelcoats used for above water application tend to have spotty blushing when shrink-wrapped during transportation and storage. The boats, when shrink-wrapped can cause moisture to be trapped between the shrink-wrap and the gelcoat. This trapped moisture, causes blushing when heated. The blushing may be temporary or permanent depending on the quality of the gelcoat used. The temporary blushing is caused by the blushing on the surface film of the gelcoat and can be removed by applying heat to the gelcoat. The permanent spotty blushing is caused by the fading of the pigments/extender pigments and cannot by recovered by any means.

Hence there is a need for developing a blush resistance gelcoat that does not fade when exposed to water and also which can withstand the blushing when exposed to moisture that is trapped between the shrink-wrap and the gelcoat.

Experiment

A study was undertaken to develop a blush resistant gelcoat. This study included the evaluation of each raw material used in the gelcoat for its contribution towards blushing. The study indicated three major contributors to the blushing phenomena: base polymer, extender and pigments. Based on these findings, a project was undertaken to develop a new polymer, and select the extenders and pigments that gave the best blush resistant performance.

Base Polymer backbone

Various permutation and combinations of the building blocks of the polymer backbone were evaluated for blush resistance properties. Mono functional, difunctional and tri-functional acids/anhydrides mono alcohols, diols and triols were used. A new chemical backbone with enhanced blush resistance characteristics was developed. This new proprietary polymer not only had excellent blush resistance properties but also had improved weather ability compared to the conventional gelcoat.

Extender Pigments

Various extenders were studied either alone or in combinations. The extenders used in the study included, but not limited to alumina trihydrate, calcium carbonate, calcium sulphate, mica, talc, micro glass hollow and solid spheres, barium sulphate and coated talc.

Pigments and additives

Various functional groups of organic pigments from different suppliers were studied. The pigment and extender levels were also varied to determine the optimum level required to give best blush resistance performance without affecting the blister and weathering performance.

Conventional and non-conventional monomers and thixotropes were used in the formulation. Additives were added to improve the air release, flow properties, filler wetting, surface leveling, pigment dispersion, viscosity stability and prevention of pigment flocculation.

A blush resistance gelcoat was developed based on the above combination. This gelcoat was studied for blush and blister resistance and weathering properties in eight different colors.

Panel preparation

Gelcoat was sprayed 22-24mils wet on a waxed glass mold using external mix spray equipment. Once the gelcoat was cured, 10mils wet of barrier coat was applied. After the barrier coat was tack free a 4 ply 1.5oz chopped strand mat was applied using DCPD ORTHO backing resin. The laminate was allowed to cure for 24hrs at ambient temperature and then post cured in an oven at 150 °F for 2hrs.

Blush and blister resistance

The gelcoat side of each panel was exposed to 185°F water in a blister box. After 100hrs the panels were evaluated for color change, gloss retention and blister rating. The panels were rated from 1-10 based on the size and numbers of blisters. Comparative results of Conventional gelcoat and the new blush resistance gelcoat is shown in Table 3 for 100 hours and in Table 4 for 200 hours.

Shrink-wrap test

A panel of 100mm X 150mm was covered with a polyethylene shrink-wrap using duct tape. 10ml of distilled water was inserted between the polyethylene wrap and the gelcoat. The wrap was then sealed with duct tape. Then panel was then placed in an oven at 140°F for 24 hours. After 24 hours the panel was checked for color and gloss. The panel was also evaluated for visual blushing of color. Results of the shrink-wrap test are shown in Table 5.

Accelerated Weathering test

Performed QUVA as per ASTM G-154 and Xenon Arc as per ASTM G-155 accelerated weathering test. Results of accelerated weathering study are shown in Table 6.

The QUVA Cycle was as follows:
4 hours condensation at 113°F and 8 hours UVA at 140°F.

The Xenon Arc exposure conditions were as follows:
Auto irradiance 0.35 W/sq.m@340nm
Black panel (BP) temperature 145°F
Cycle 102 mm light followed by 18min light and water spray repeating 24h/d
Relative humidity: Light only cycle: 50 $\pm$ 5% + water spray: 95 $\pm$ 5%.

The new blush resistant gelcoat was also evaluated for its application parameters. The gelcoat was sprayed on a marine personal watercraft mold. The application parameters are shown in Table 2

Results and Discussion

Typically low VOC gelcoat, due to their high cross link density and lower molecular weight, exhibits a tensile elongation of 1.3 to 1.8%. The new blush resistant gelcoat has excellent flexibility with a tensile elongation of greater than 2.5%. This higher elongation of the new gelcoat is attributed to the novel modification of the backbone of the polymer used in the gelcoat. Results in Table 2 indicate that the blush resistant gelcoat is easy to use and provides porosity free film under normal application conditions.

One of the salient features observed with this gelcoat was its excellent sanding, buff back and repair properties. Conventional low VOC dark colored gelcoat exhibits poor buff back with ghosting and hallowing after repair. The blush resistant gelcoat gave a hard surface on curing, which was easy to sand, buff and patch without any ghosting or hallowing.

The blister test results indicate that the new blush resistant gelcoat has excellent blister resistance when used with a vinyl ester barrier coat. Results for the blush test in Table 3 and 4 indicate that the new blush resistant gelcoat exhibit far superior color retention on exposure to water at 185°F for 100 and 200 hours. The conventional low VOC gelcoat faded especially in dark colors. The light colors like yellow and orange did not have significant blushing. Also, the new gelcoat did not show any blushing for shrink-wrap test. The conventional Low VOC gelcoat showed significant blushing in dark colors. The improvement in the blush resistance properties of this gelcoat is attributed to the hydrophobic properties of the resin, lower water absorption characteristics of the extender pigments and the fade resistance properties of the pigments/extender pigments used in this gelcoat. Accelerated weathering properties results in Table 6 indicate that the new gelcoat has excellent weathering properties required for the Marine application.

Conclusion

This work has led to the development of blush resistance gelcoat for the marine industry. This new gelcoat has excellent application and performance properties. It will prove extremely valuable to the Marine industries as well as for the Transportation and Recreational Vehicle Industries.

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BIOGRAPHIES

Ranjit Pachha

Ranjit Pachha received his Ph.D in Polymer chemistry from Sardar Patel University, India in 1995. He has seven years experience working in the composites industry. He joined Valspar in the year 2001 and has been involved in the development of unsaturated polyester resins and gelcoats.

Brian Robertson

Brian Robertson is the North American Technical Manger of Valspar Composites for new product development. He has been with Valspar since 1985. His areas of expertise are polymer synthesis, resin and gelcoat development. Brian has developed numerous proprietary unsaturated resin and gelcoat technologies for all composites markets.

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Len Pulman is the Technical Manager of Valspar Composites for specialty products. He has been with Valspar since 1990 and has over 35 years of experience in polymer synthesis, resin and gelcoat development. Len has been instrumental in the development of blush resistant gelcoats, cultured marble clear gelcoats, high performance bonding adhesives, marine and transportation gelcoats.

Richard Chang

Richard Chang is the Director of Quality and Technology of Valspar Composites. He has been with Valspar since 1999 and is responsible for new technology development, introducing innovative products to the composites industry and implementing several unique quality assurance initiatives.

Table 1 Physical properties of the liquid and cured Gelcoat

	Properties	Values
Properties in Liquid form	Solid Content	65-68%
	HAPS Content	30-33%
	Viscosity Spd #4 2RPM	22000-38000cps
	Viscosity Spd# 4 20RPM	4000-5500cps
	Gel time at 77°F 1.5% DDM-9	18± 2 minutes
	Gel to Peak time	8± 2 minutes
Properties of the Cured Product (Gelcoat only)	Tensile Strength, psi	8961
	Tensile Modulus, ksi	508.33
	Elongation at Break, %	>2.5
	Flexural Strength, psi	15686
	Flexural Modulus, ksi	504
	Mandrel Elongation ½ Inch strip of 17mils Dry thickness after 24hrs	1/2inch
	HDT	140°F

Table 2 Application Parameters

Equipment Type	HVLP
Tip size	521,523, 621, 623
Pump ratio	20-1
Pump pressure	60
Atomizing pressure	25
Air Assist	1/4turn
Inline Heater	6.0
Catalyst Feed	Slave
Catalyst Type	Methyl ethyl ketone peroxide
Catalyst percentage	1.5
Fingers	None
Surface Porosity, dry mils	>50
Sub porosity, dry mils	>35
Sanding	Good, no clogging of sandpaper
Buff back	Excellent, no hazing on any colors
Repair	Excellent, No hallowing or patch marks

Table 3 Blister and Blush Test properties after 100 hours

Panels	Initial Gloss	MACT compliant Blush resistance gel-coat				MACT compliant conventional gelcoat			
		Blister Rating	Color Change ΔE	60° Gloss	Visual Change	Blister Rating	Color Change Δ E	60° Gloss	Visual Change
Flag Blue/	95.7	10	.34	92.6	No blush-ing	10	10.18	90.6	Blushing
Midnight Blue	94.3	10	.30	91.3	No blush-ing	10	5.41	89.7	Blushing
Red 5R-54	96.5	10	1.24	92.3	No blush-ing	10	2.24	91.8	Slight blushing
Yellow 5L-55	93.8	10	.44	91.4	No blush-ing	10	1.73	93.4	Slight blushing
Mist Green	95.1	10	.42	92.7	No blush-ing	10	18.38	86.3	Blushing
Black	94.8	10	.28	93.6	No blush-ing	10	1.27	89.8	Blushing
Deep Purple 5R-42	93.6	10	.17	91.8	No blush-ing	10	10.4	87.8	Blushing
Orange 5N-12	95.2	10	.55	90.0	No blush-ing	10	3.06	91.2	Slight blushing

Note 1: Blister Rating Scale 1-10, 10 indicating panel free of fiber print and blisters.

Table 4 Blister and Blush Test results for 200hours

Panels	Initial Gloss	MACT compliant Blush resistance gelcoat				MACT compliant conventional gelcoat			
		Blister Rating	Color Change Δ E	60° Gloss	Visual Change	Blister Rating	Color Change Δ E	60° Gloss	Visual Change
Flag Blue/	95.7	10	.66	85.9	No blush-ing	10	12.3	86.3	Blushing
Midnight Blue	94.3	9	.55	86.3	No blush-ing	10	7.28	87.9	Blushing
Red 5R-54	96.5	9	1.57	92.1	No blush-ing	10	3.51	88.9	Slight blushing
Yellow 5L-55	93.8	9	1.03	87.8	No blush-ing	10	2.12	90.6	Slight blushing
Mist Green	95.1	9	.58	87.3	No blush-ing	10	19.26	85.7	Blushing
Black	94.8	10	.72	92.4	No blush-ing	10	2.89	92.5	Blushing
Deep Purple 5R-42	93.6	10	.19	90.3	No blush-ing	10	13.65	85.7	Blushing
Orange 5N-12	95.2	10	.53	89.6	No blush-ing	10	5.23	88.3	Blushing

Note 1: Blister Rating Scale 1-10, 10 indicating panel free of fiber print and blisters.

Table 5 Shrink Wrap test results

Panels	Initial Gloss	MACT compliant Blush resistance gelcoat			MACT compliant conventional gelcoat		
		Color Change Δ E	60° Gloss	Visual Change	Color Change Δ E	60° Gloss	Visual Change
Flag Blue	95.7	.12	90.6	No change	1.85	91.5	Spotty blushing
Midnight Blue	94.3	.08	93.2	No change	2.10	89.5	Spotty blushing
Red 5R-54	96.5	.35	91.6	No change	2.27	85.6	Spotty blushing
Yellow 5L-55	93.8	.32	91.8	No change	.45	90.8	No change
Mist Green	95.1	.06	92.1	No change	1.31	89.7	Spotty blushing
Black	94.8	.26	89.6	No change	3.15	87.4	Spotty blushing
Deep Purple 5R-42	93.6	.12	88.6	No change	1.02	90.8	Spotty blushing
Orange 5N-12	95.2	.18	95.6	No change	.65	91.5	Minor blushing

Table 6 Accelerated Weathering Test results

Panels	Initial Gloss	QUVA				Xenon Arc			
		1000 Hrs		1500Hrs		1000Hrs		1500Hrs	
		Δ E	60° Gloss	Δ E	60° Gloss	ΔE	60° Gloss	Δ E	60° Gloss
Flag Blue	95.7	.46	92.3	.56	89.5	.14	80.9	.19	78.9
Midnight Blue	94.3	.78	94.4	.98	88.3	1.50	85.3	1.76	82
Red 5R-54	96.5	.89	90.3	2.0	88.7	1.88	85.4	1.94	82.7
Yellow 5L-55	93.8	1.19	94.3	1.14	89.2	1.42	89.2	1.83	87
Mist Green	95.1	.30	93.8	.35	87.7	.29	88.4	.35	82.3
Black	94.8	-.20	94.3	.35	88.8	.07	88.1	.61	76
Deep Purple 5R-42	93.6	.30	93.8	1.12	84.6	1.43	87.1	1.58	84
Orange 5N-12	95.2	1.19	94.3	.47	89.6	.08	89.1	.46	87.7

FIG 1:BLUSH TEST PANELS AFTER 100 HOURS AT 85C

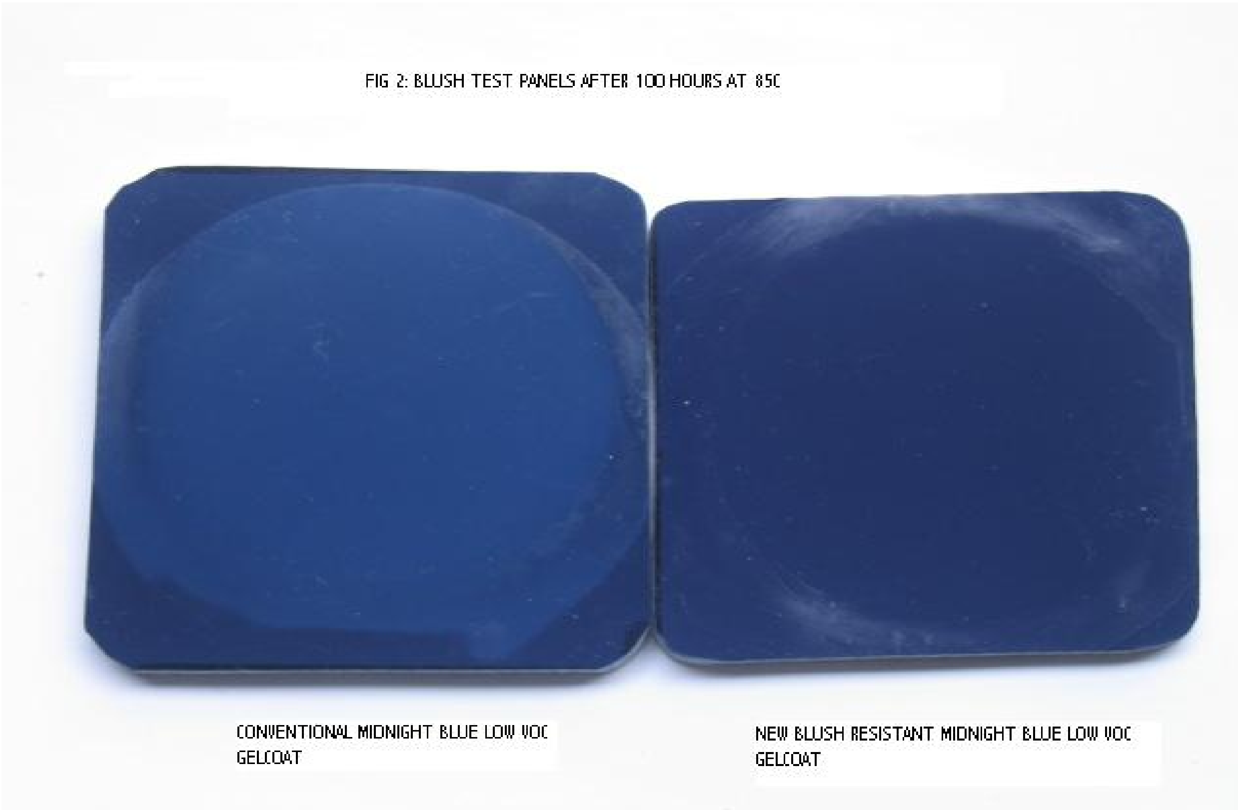

FIG 2: BLUSH TEST PANELS AFTER 100 HOURS AT 85C

FIG 3: BLUSH TEST PANELS AFTER 100 HOURS AT 85C


FIG 3: BLUSH TEST PANELS AFTER 100 HOURS AT 85C
CONVENTIONAL MIST GREEN LOW VOC GELCOAT
NEW BLUSH RESISTANT MIST GREEN LOW VOC GELCOAT