Technical Research

CoREZYN Premium Vinyl Ester Molecule

A 15-Year Study of the Effective Use of Permeation Barriers in Marine Composites to Prevent Corrosion and Blistering

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ABSTRACT

Accelerated blister testing at elevated temperatures has been used for many years as a tool to assess the performance of gel coats and resins in marine and swimming pool applications. However, the use of the accelerated testing has been questioned over the years since the actual application is under ambient conditions. The accelerated testing exposes the resins and gel coats to a combination of heat and water. This combination may cause premature failure due to heat and not the water. This work sets out to compare long-term ambient exposure to short-term elevated temperature exposure.

The immersion study that began in 1986 on gel-coated panels and castings at ambient temperatures continued for 15 years. This paper presents the data collected on the various composites over this 15-year period with an emphasis on the comparison of ambient temperature testing to the accelerated testing.

The second part of this presentation looks at ASTM D 570 water absorption studies on clear castings at ambient and elevated temperatures accomplished side-by-side with the gel-coated panel study.

INTRODUCTION

Marine and swimming pool manufacturers have used elevated temperature testing [1,2,3,4] as a tool to screen the blister performance of gel coats and resins for many years. Results from the elevated temperature testing have been questioned over the years since the actual application is at ambient conditions, not hot water exposure. One of the main arguments made against elevated temperature testing was that it was being run above the resin's heat distortion or glass transition temperature. The elevated temperature was thought to either weaken the resin or change the water transfer mechanism in the composite, causing it to blister prematurely.

Interplastic Corporation presented a study in 1987[5] that used a unique construction of gel-coated panels, as well as resin castings in blister resistant tests. The results pioneered the use of vinyl ester resins as a corrosion or blister barrier in the marine and swimming pool composite markets. This study compared the performance of panels at 200°F (93°C), 150°F (65°C) and at ambient temperature exposures for a period of over 200 days.

That work was the springboard for using vinyl ester resins and vinyl ester-polyester blends in the marine, swimming pool and spa composites manufacturing industries. Blistering went from a major warranty issue to a minor, or even a non-existent one, for the companies that incorporated vinyl ester or vinyl ester-polyester blends in their composites. When their composite has been properly constructed, many of these boat manufacturers have gone more than ten years, and some more than 15 years, without a warranty claim because of blistering.

EXPERIMENTAL

Three resins were used in the study. The CoREZYN® CORVE8117 thixotropic vinyl ester resin, commonly used in marine composite applications, and hereafter referred to as the vinyl ester. A two-stage isophthalic resin, designed for corrosion applications was selected and an orthophthalic resin that was typically being used in the marine market at the time. Their physical properties are listed in Table 1.

each constructed with fiberglass and resin at a 1:2 ratio. Each of the resins was catalyzed with 1.5% of 9% active oxygen MEKP containing a high dimer content. Each gel-coated plate was laminated with four plies of ¾-ounce (230 gram/m^2) chopped strand fiberglass mat. The panels were pressed together before they gelled taking care to minimize the entrapped air.

Table 1: Structural Properties of Resins					
	ASTM	Units	Orthophthalic	Isophthalic	Vinyl Ester
Flexural Strength	D 790	psi	16,300	18,500	16,900
		MPa	112.4	127.6	116.6
Flexural Modulus	D 790	psi	545,000	518,000	438,000
		MPa	3,760	3,570	3,020
Tensile Strength	D 638	psi	8,600	10,300	11,500
		MPa	59.3	71.0	79.3
Tensile Modulus	D 638	psi	632,000	565,000	446,000
		MPa	4,360	3,900	3,080
Tensile Elongation	D 638	%	1.5	2.0	6.0
Heat Distortion	D 648	°F	163	188	222
		°C	73	87	106
Glass Transition		°F	145	201	232
		°C	63	94	111
Cured 1/8 inch (3.25mm) thick clear casting.					

CASTING CONSTRUCTION

The three resins were catalyzed with 1% of 9% active oxygen MEKP, and then poured between two pieces of glass with a 1/8-inch-thick (0.32 mm) spacer to produce the castings. The castings were allowed to cure for 16 hours at ambient temperatures and then post-cured at 250°F (121°C) for two hours.

GEL-COATED PANEL CONSTRUCTION

Two panels were gel-coated on both sides. A premium, NPG®-isophthalic white gel coat was catalyzed with 2% of 9% active oxygen MEKP (Methyl Ethyl Ketone Peroxide), then drawn down to 20 mils thick by eight inches wide, on two plates of glass, and cured for two hours.

The next step was making the laminates, which were

SKIN-COATED LAMINATE CONSTRUCTION

The set of panels we constructed with a vinyl ester skin coat had an additional step.

The glass plates were first gel-coated and then cured for two hours. To construct the laminate, the vinyl ester was catalyzed with 1.75% by weight of 9% active oxygen MEKP containing a high dimer content. Then, two plies of ¾-ounce (230 gram/m^2) chopped strand fiberglass mat and the vinyl ester resin, at a 1:2 ratio; approximately 30 mils thick (0.76 mm) were put down. The vinyl ester laminate was allowed to cure until it reached a measured hardness of 5-20 using a Barber Coleman 934-1 impresser gauge.

The center reinforcing laminate was built of orthophthalic resin catalyzed with 1% of 9% active oxygen MEKP. This was followed by two plies of ¾-ounce chopped strand fiberglass mat and

orthophthalic resin at a 1:2 ratio. It was laid up on the vinyl ester skin coat and then the two panels were compressed before they gelled, taking care to minimize entrapped air.

Non-Gel-Coated, Non-Skin Coated Panels

The set of panels constructed with an orthophthalic resin and no gel coat were also made directly on the glass plates. The laminate was made with chopped strand fiberglass and resin, at a 1:2 ratio. After the glass plate was prepared, it was laminated with four plies of ¾-ounce (230 gram/m^2) chopped strand fiberglass mat. The panels were pressed together before they gelled, taking care to minimize entrapped air.

Finishing Technique

All of these panels were allowed to cure for 16 hours at ambient temperatures. Then they were cut into 5.5-inch (14 cm) square panels and their edges were coated with a thin layer of vinyl ester to seal them and eliminate the possibility of water wicking into the laminate while immersed. These edge-coated panels were allowed to cure for 16 hours and then post-cured at 250°F (121°C) for two hours.

Test Conditions

All the panels were totally immersed in a container filled with tap water. The panels were spaced to allow the water to move freely between their surfaces.

A modified version of ASTM D 570 was used for the absorption study. The weight gains of the standard composite specimens at ambient temperatures were recorded periodically over a 15-year period. Weight gains at the elevated temperatures were recorded over 200 days.

For the elevated temperature immersion testing, the containers were maintained at the specified temperatures of 150°F (65°C) and 200°F (93°C), [±2°F (+1°C)], for the 200-day test period.

The ambient temperature immersion test was as "real world" as possible with the test temperatures ranging

as high as 90°F (32.2°C) in the summer months, to 50°F (10°C) during the winter. The typical temperature range for a majority of the 15-year test was 65-80°F (18-27°C).

When the coupons were removed from the water at inspection times, they were patted dry with an absorbent cloth and allowed to cool to room temperature. Once they reached room temperature and allowed to adjust to ambient conditions, each specimen was weighed and then re-immersed in its appropriate container. At various intervals, one of the coupons from each set was removed and tested for a variety of properties such as wet physical properties, weight loss after drying, dry physical properties and glass transition temperature.

RESULTS AND DISCUSSION

Heat Distortion, Glass Transition and Blister Formation

The heat distortion and glass transition temperatures for these products are listed in Table 1.

The ambient testing was below the heat distortion and glass transition temperatures of all three resins. This eliminated the concerns that exceeding these temperatures does not represent actual use conditions.

The elevated temperature (200°F/93°C) and (150°F/65°C) and the ambient temperature testing were below the heat distortion and glass transition temperatures of the vinyl ester.

The elevated temperature testing and ambient temperature testing were below the glass transition temperature of the isophthalic resin but the test conducted at 200°F (93°C) was above its heat distortion temperature.

The heat distortion and glass transition temperatures of the orthophthalic resin were below the 200°F (93°C) and 150°F (65°C) testing. If the concerns about testing above the heat distortion and/or glass transition were true, the orthophthalic resin would have had different results relative to that of the vinyl ester and isophthalic resins at the two elevated temperatures. This is not what we observed.

Table 2 shows the time it took for blisters to form for each of the gel-coated composites, at each of the temperatures.

The orthophthalic coat blistered the fastest at all three temperatures; the isophthalic composite followed.

The vinyl ester was the last to blister at 200°F (93°C), and it did not show any signs of blistering at 150°F (65°C) or at ambient conditions.
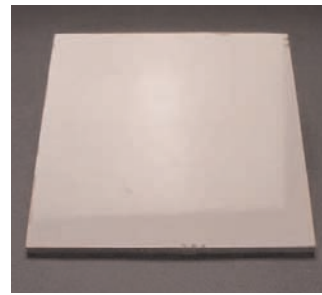
The vinyl ester panel at 15 years.

Another interesting finding was that at all three temperatures, the orthophthalic laminate constructed with a vinyl ester skin coat had very similar time-to-blister formation results as the 100% vinyl ester panel.

Table 2: Time For Blisters to Form in the Gel Coat at Various Temperatures.			
Test Temperature **Composite**	**200°F (93°C)**	**150°F (65°C)**	**60-90°F (15-32°C)**
Orthophthalic Laminate	**25-50 hours**	**15 days**	**1.6-5 years**
Isophthalic Laminate	**75-100 hours**	**21 days**	**5-10 years**
CORVE8117 Laminate	**175-200 hours**	**>300 days**	**>15 years**
CORVE8117 Skin Coat Orthophthalic Laminate	**250-300 hours**	**>300 days**	**>15 years**

WEIGHT INCREASES AT AMBIENT TEMPERATURES

Table 3: Ambient Water Absorption of Laminates at Ambient Temperature				
Time (days)	Orthophthalic w/o Gel Coat	Orthophthalic Laminate	Isophthalic Laminate	Vinyl Ester Laminate	Vinyl Ester Skin Coat Orthophthalic Laminate
1	0.03	0.03	0.05	0.11	0.05
2	0.07	0.08	0.08	0.15	0.07
3	0.08	0.09	0.09	0.16	0.08
4	0.12	0.12	0.14	0.18	0.13
14	0.16	0.16	0.16	0.23	0.12
21	0.18	0.20	0.21	0.26	0.16
35	0.22	0.24	0.26	0.29	0.22
49	0.25	0.27	0.29	0.32	0.22
70	0.36	0.39	NR	0.40	0.22
98	0.38	0.40	0.50	0.39	0.42
140	0.44	0.48	0.50	0.46	0.43
203	0.57	0.58	0.59	0.53	0.52
273	0.65	0.70	0.65	0.57	0.59
420	0.67	0.68	0.67	0.59	0.65
616	0.79	0.76	0.68	0.58	0.74
3640	1.06	1.05	0.75	0.58	0.97
5670	1.29	1.19	0.78	0.52	1.10
Percent weight gain on gel-coated laminates and on orthophthalic laminate without gel coat.				

The weight changes on the five sets of gel-coated panels tested at ambient temperatures were monitored for the 15-year test period. The data is compiled in Table 3 and illustrated in Figure 1. The graph is plotted on a semi-log form, with "Log of Time" on the X axis and "Percent Change" on the "Y" axis.

The isophthalic gel-coated, orthophthalic non-gel-coated, and orthophthalic gel-coated panels had similar absorption rates over the first 420 days. The curves show a slight inflection at 140 days, where the rate of weight started to increase for all three panels. The least square analysis of the initial 49 days of data is compiled in Table 4.


The orthophthalic panel after 15 years.

The orthophthalic non-gel-coated and orthophthalic gel-coated panels continued to gain weight over the 15-year test. Figure 1 shows these two composites virtually had identical weight change percentages over the 15-year test. Blisters formed on the orthophthalic gel-coated panel between 1.75 and 5 years.

Table 4: Curve Fit Analysis of Ambient Temperature Gel-Coated Panels			
Composite	Slope	Intercept	Correlation
Orthophthalic no gel coat	0.127	-0.158	0.951
Orthophthalic laminate	0.137	-0.171	0.948
Isophthalic laminate	0.142	-0.171	0.945
CORVE8117 laminate	0.117	-0.0634	0.937
CORVE8117 skin coat Orthophthalic laminate	0.111	-0.120	0.909
A semi-log least square regression analysis of the water absorption data on the initial 49 days of exposure. All the panels had gel coat on two sides except for the orthophthalic panel noted above.			

Figure 1: Weight Gain of Gel-Coated Panels Immersed in Ambient Water
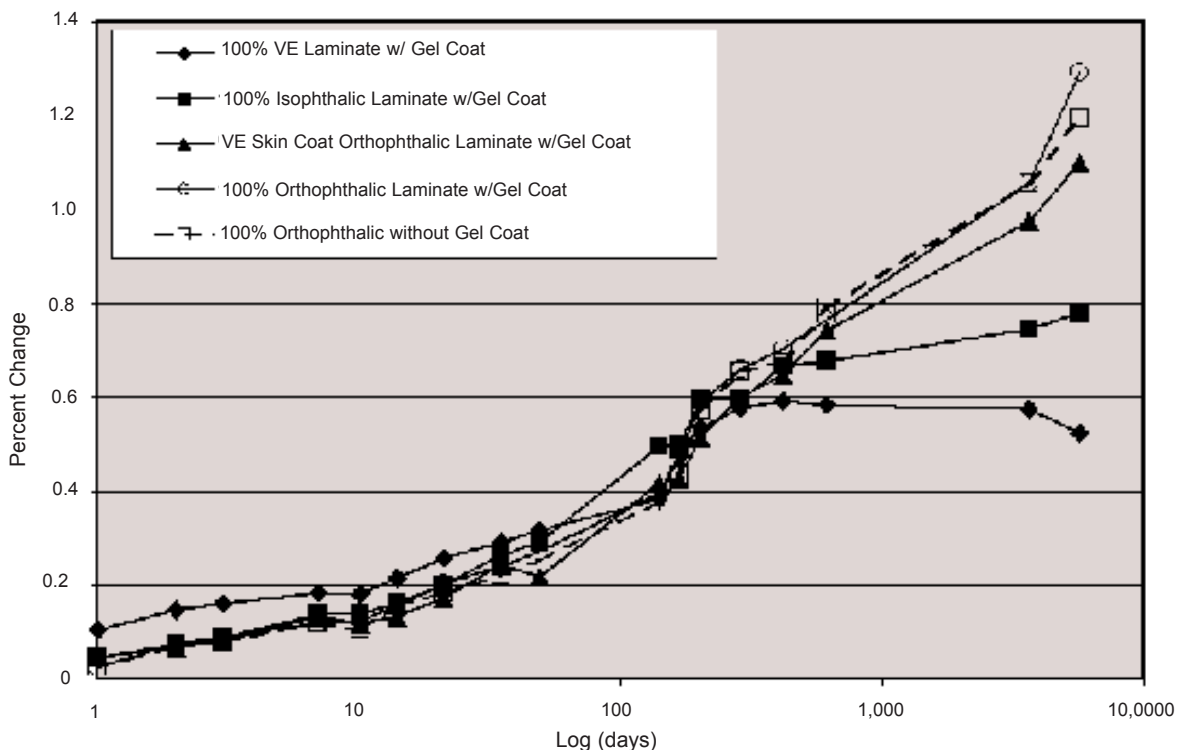
The gel-coated isophthalic panel's weight gain started to diverge from the group between 203 and 273 days, when its rate of absorption slowed. Even though its rate of weight increase began decreasing, it still gained weight over the 15 years of testing. Blisters were not visible on this set of panels at the 5-year point but they were there at the 10-year observation.
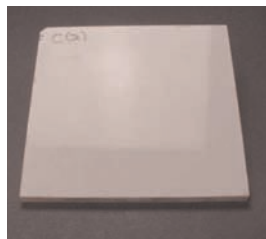
The gel-coated isophthalic, panel after 15 years

The vinyl ester gel-coated composite had a faster initial water absorption compared to the other three panel constructions, which can be seen in the percent weight gain after one day. However, the other three panels surpassed the vinyl ester panel between 140 and 203 days in overall percent weight gain. The vinyl ester panel reached a plateau of 0.56% around day 203 and it maintained that level over the 15-year test period.

The orthophthalic gel-coated panel with a vinyl ester skin coat had a similar rate of weight increase as the isophthalic gel-coated, orthophthalic non-gel-coated and orthophthalic gel-coated panels over the first 420 days. The rate of weight increase for the isophthalic gel-coated panel compared to the orthophthalic

composites began to slow between 1.75 and 10 years.

The weight of the orthophthalic vinyl ester skin-coated panel continued to climb throughout the 15 years. However, this set of panels showed no signs of blisters at the end of the test period.

WEIGHT GAIN OF CASTINGS USING MODIFIED ASTM D 570

The modified ASTM D 570 water absorption study was run at 200°F (93°C) for 14 days. Weight change data collected from the resin castings is compiled on Table 5 and shown on Figure 2. The gel coat polymer (NPG-iso) data is shown there as well.

The vinyl ester castings started to plateau in two days.

The orthophthalic casting had more than a 2.5% gain after four days and then showed a weight loss on the seventh and fourteenth days. This means that the polymer is being broken down, solubilized, leached out of the composite and replaced with water.

The isophthalic casting continued to gain weight over the 14-day period.

The NPG gel coat castings reached their plateau between days four and seven.

Table 5: Weight Gain Measured According to Modified ASTM D 570				
Time (days)	Vinyl Ester	Orthophthalic	Isophthalic	Neopentyl Glycol Isophthalic Acid
0.33	0.66	1.25	0.59	0.61
0.66	0.81	1.49	1.01	1.05
1	0.94	1.84	1.19	1.25
2	1.21	2.26	1.36	1.64
4	1.24	2.73	1.47	1.95
7	1.27	<0	1.75	2.05
14	1.26	<0	2.30	2.09
Percent weight gain at 200° (93°C) on 2 x 2 inch (5.1 x 5.1 cm) clear casting coupons.				

Modified ASTM D 570 on Vinyl Ester Castings Only

The modified ASTM D 570 water absorption was run at the three temperatures only on the clear castings of the vinyl ester. The least square analysis is compiled in Table 6 and plotted in Figure 3.

The initial rates of weight increase for the vinyl ester, at each temperature, were analyzed with a least square plot to determine the water absorption rate. The data was analyzed with a semi-log, least square regression of the ambient temperature data for the initial 49 days of exposure. The 150°F (65°C) analysis used the points from the initial 21 days. Finally, the 200°F (93°C) analysis used the data collected over the first two days. The least square correlation factors were excellent for all three sets: 0.965, 0.932 and 0.979 respectively. The plateau levels reported in Table 6 were determined based on the remaining points from each set.

The modified ASTM D 570 water absorption tests at room temperature showed the vinyl ester panels reached a plateau around 70 days and maintained that weight over the next 15 years. Analyzing the data from the first 70 days with a semi-log least square analysis shows a correlation factor of 0.965.

The ASTM D 570 water absorption for the coupons at 150°F (65°C) plateau around 35-49 days and they maintained that weight gain for over the remaining 200 days. Analyzing the data for the first 21 days with a semi-log least square analysis shows a correlation factor of 0.932. The water absorption for the coupons at 200°F (93°C) plateau at two days and they maintained that weight gain for at least 147 days. Analyzing the data from the first two days with a semi-log least square analysis shows a correlation factor of 0.979. Table 6 contains the data.

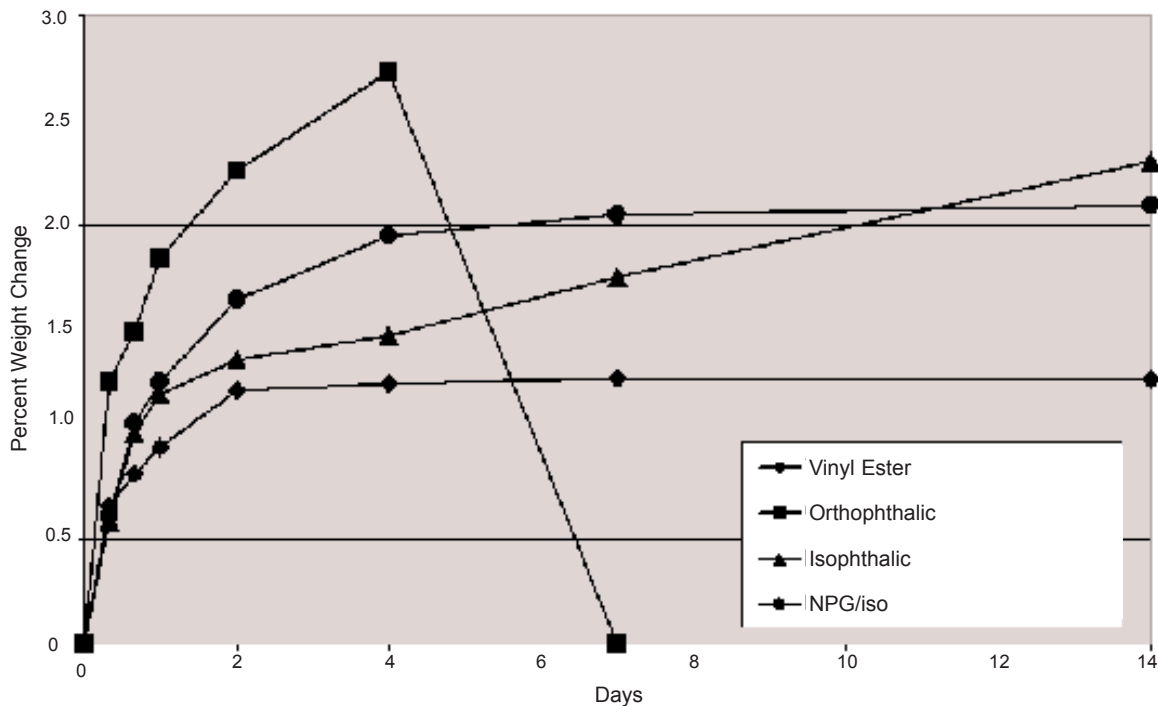Figure 2: Casting Weight Gain at 200°F (93°C) of 4 Polymers

Table 6: Analysis of Vinyl Ester Water Immersion Data				
Temperature	Slope	Intercept	Correlation	Plateau
Ambient	0.282	-0.219	0.965	0.7792
150°F (65°C)	0.351	0.106	0.932	1.0185
200°F (93°C)	0.710	-0.011	0.979	1.2368
A semi-log least square regression analysis of the ASTM 570 water absorption data for the vinyl ester. The initial 49 days of exposure for the coupons exposed to ambient temperatures were used for the least squares analysis. The initial 21 days of exposure were used for the 150°F (65°C) least squares analysis. The initial two days of exposure were used for the 200°F (93°C) least squares analysis. Reported plateau is an average of the day 70 to year 15 data.				

Figure 3: Casting Weight Change for Vinyl Ester at 3 Temperatures
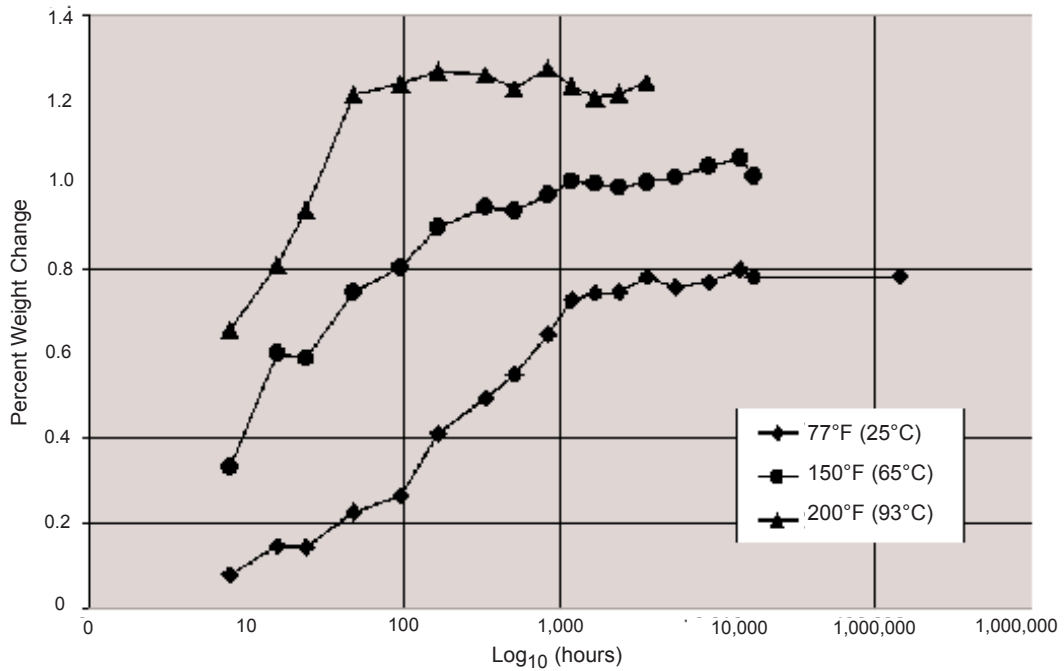
FOOTNOTES

1. Edwards, H. R., "Variables Influencing the Performance of a Gel Coated Laminate," 4th Annual Conference, SPI Reinforced Plastics/Composite Institute.

2. Crump, S. "A Study of Blister Formation in Gel Coated Laminates," 41st Annual Conference, SPI Reinforced Plastics/Composite Institute.

3. Adams, R. C. "Variables Influencing the Blister Resistance of Marine Laminates," 37th Annual Conference, SPI Reinforced Plastics/Composite Institute.

4. Hewitt, J. "Evaluation of the Factors that Influence the Blister Resistance of Boat Hulls and Methods Used to Test Them," Composites 2001.

5. Burrell, P., Herzog, D., McCabe, T. "A Study of Permeation Barriers to Prevent Blisters in Marine Composites and a Novel Technique for Evaluating Blister Formation," 42nd Annual Conference, SPI Reinforced Plastics/Composite Institute.

REFERENCE

This work is based on the original technical paper of the same title, published in 2002, by David J. Herzog and Paul P. Burrell, on behalf of Interplastic Corporation. It is available from the American Composites Manufacturing Association (ACMA).

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