



Evaluation Of The Factors That Influence The Blister Resistance Of Boat Hulls and The Methods Used To Test Them

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ABSTRACT

This paper examines the influence that resin, gel coat, and fiberglass have on the formation of osmotic blisters in boat hulls. Laminates made with polyesters (PE) resins, vinylester (VE) resins, VE blends, and a new modified polyester (MPE) resin were compared. The comparative effectiveness of using a barrier coat vs. a skin coat was also examined. The influence that the various laminate components have on the blister results was also examined. Different types and thickness of gel coat were evaluated. The impact that fiberglass and the sizing and/or binders on the fiberglass have on blister formation were also examined.

A comparative analysis was made of the various methods used to test the blister resistance of a composite. We compared the 212°F/100°C boiling water test to tests run at 150°F/65°C and at 100°F under 18psi water pressure. Gel coated, non-gel-coated, reinforced, and non-reinforced coupons will be compared. These different testing methods were compared for their reproducibility of results and their potential to predict actual blister resistance in the field, to determine which test methods are the best to evaluate resins.

BACKGROUND AND OBJECTIVES

Resistance to the formation of osmotic blisters is a very important attribute for composites that will be exposed to water for extended periods, such as boat hulls. Most fabricators of such parts require some assurance of the blister resistant properties of their resin and/or gel coat before using them in their parts. They may use various blister tests to evaluate their composite, compare types of material, or to compare similar products from different suppliers. As often is seen with testing in the composite industry, there are many

different methods used to evaluate the blister resistance of a composite and to compare the impact different materials used in the composite have on blister formation. In this work we investigated the effectiveness and accuracy of the various test methods used to evaluate blister resistance. We also looked at the effect various components used in the composite have on blister resistance.

Also of interest in this study, was a comparison of vinylester barrier coats and a new modified polyester resin skin coat to the resins currently being used in the marine industry for improved blister resistance of boat hulls. As a secondary objective we wanted to evaluate the effect gel coat type and thickness have on blistering along with determining the influence the glass reinforcement has on blister formation. Since we wanted to be assured of the reliability of our results, we tested these materials under different test conditions and laminate fabrications and then compared the results.

MATERIALS TESTED

Traditionally VE and VE/PE blended resins have been use to provide blister resistance in boat hulls. Because of their higher cost, these VE and VE/PE blended resins are primarily use only in the first layer of glass applied directly behind the gel coat of the hull. This layer is often referred to as the “skincoat”. The VE/PE blends currently used in the marketplace vary from products composed primarily of VE resin with only a small percentage of PE resin to those products that are composed of primarily PE and may contain 20% or less VE. The blends containing low levels of VE resin are used mostly in shops that prefer to use one resin for the entire boat construction but want some increased blister resistance. To manage cost,

they use the products with lower levels of VE resin. Since the VE resin is the material in these blends that is providing the blister resistance, a reduction in VE resin level can reduce the resistance of the composite to blisters.

In looking at methods to improve the blister resistance of a polyester resin, we examined the chemical structures of a VE resin that gives it such good blister resistance. Modifications were made to a PE resin to give it some of these same properties, but at a much lower cost. We wanted to see how this resin compared to the VE/PE blends, in particular the ones with the lower level of VE it would replace.

Another solution to the two-resin issue, that has become more popular recently, is a VE barrier coat. The barrier coat is applied like a gel coat directly behind the exterior gel coat. A glass layer using a PE resin is then applied in back of this barrier coat. The barrier coat has been performing very well in the field, so it provides a good benchmark, along with the skin coats made with VE and VE/PE blends, for our testing. To provide other benchmarks we also included in the testing general purpose orthophthalic, DCPD, and isophthalic based polyester (PE) marine resins. To provide a cross section of resins sold into the marine industry, we included resins currently marketed by AOC and by other resin suppliers. We also tested resin blends made in the lab. A list of the products tested and a short description of those products are shown in Figure #1.

The product labeled PE modified VE is almost all VE with a small amount of PE added. The products labeled VE/PE blends, contain nearly equal amount of VE and PE resins. Those products labeled VE modified PE resin contain mostly polyester with some VE added. We included resins containing varying amounts of styrene in the testing. While this list by no means included all products sold into the marine market, it does provide a good cross section of the major types of products being sold into this market.

While it was not the main focus of our study, we also looked at the impact fiberglass and fiberglass types have on blistering. Since most of our tests were run with laminates made using fiberglass mat, we needed to have a complete picture

of the influence fiberglass has on blister formation. We ran tests on laminates using gun roving, mat, and fiberglass with the sizing and binder removed.

Since a majority of our testing was performed with laminates made with a gel coat, we felt it was necessary to evaluate the effects of gel coat type and thickness on some of the laminates tested. Our objective was not the evaluation of the blister resistance of gel coat. We only needed to determine the impact the gel coat was having on our test results. We ran two types of gel coat using three different thickness of each.

TEST CONDITIONS

As often is seen with testing in the composite industry, there are many different methods used to evaluate the blister resistance of a composite. These tests are being run to compare different types of resins and/or gel coat or to compare similar type products from different suppliers. In this work we investigated the effectiveness of many different test methods and procedures.

For a blister test to have value it needs to address the follow questions:

- 1) Repeatability
 - a) Will test produce the same or similar results with the same coupon tested at different time?
 - b) Will test produce the same or similar results when the same materials are used to make a different test coupon?
 - c) Will the ranking or rating of the coupons remain the same or similar from one test to another?
- 2) How well does the test predict actual performance the field?
- 3) How much time is required to get test results that will differentiate between products?
- 4) Is the test being use to evaluate total composite or individual components of the composite?

We ran the following tests:

- 1) 212 °F/100 °C Ambient Pressure
 - a) Laminates with gel coat
 - b) Laminates without gel coat
 - c) laminates with glass cloth and no gel coat

- d) Castings made with resins containing various thixotropes
- e) Castings made with resins containing no thixotrope
- 2) 150°F/40°C Ambient Pressure
 - a) Gelcoated laminates
 - b) Castings made with resins containing various thixotropes
 - c) Castings made with resins containing no thixotrope
- 3) 100°F/38C 18psi water pressure
 - a) Gelcoated laminates

Steel boxes with holes cut in the sides to allow for one-sided exposure of the coupon to the water were used to run the tests. The boxes used for testing at 212°F and 150°F test were heated with a hot plate. (Figure #2) The box used for testing at 100°F with 18-psi water pressure (Figure #3) was placed in a room with a constant 100°F room temperature. (Figure #4)

One of the parameter of testing we had to determine, was how long to run each test. If a test is run for a shorter period of time, most of the high quality resins will have very little blister formation. Differences in the effect these resins have on blistering will be difficult to distinguish. If the coupon exposure is too severe, a majority of the coupons will look equally bad. At the point of 80-90% coverage of the coupon surface, the blistering does not get much worse with additional exposure. The amount of time the coupons are exposed must not be so great that a large number of coupons have more than 80% blister coverage.

The time needed to evaluate standard products will be less than that needed to differentiate premium blister resistant products. Castings of all products and the premium products, in particular, go much longer before blister formation than do laminates (gel coated or non-gel coated) made with the same resin. The time periods used in our testing varied from as little as 50 hours with the boil tests of gel coated panels to over 2000hrs with some of the lower temperature tests.

TEST COUPONS

We made the laminate coupons by drawing down gel coat onto a glass plate using a 20 mil-draw down bar. A 20 mil-draw bar will deposit 17mils of wet gel coat, which will cure to a thickness of 12-

13 mils. (Note: Testing done with gel coat sprayed on the glass plate did not show any appreciable difference in blistering from the panels made with drawn gel coat) For the coupons using the barrier coat we applied a wet film of 12 mil of the barrier coat directly behind the gel coat while the gel coat was still wet.

After the gelcoat and barrier coats were allowed to gel and cure to a tack free state, a 2oz skin-coat, using 2% MEKP was applied to the gelcoat/barrier coat. Two hours after the start of the skin-coat application the build-up laminate was applied, with 1.25% MEKP, behind the skin coat using 3 plys of 2 oz mat. The laminates were removed from the glass plate the following day. After allowing for 48 hrs of room temperature post cure, the laminates were put in an oven at 150°F/45°C for 4 hour to complete the post cure. Each panel was cut up into coupons to a size that would fit on the tester. These coupons were than used to run multiple tests on our three test boxes. The casting coupons were made by mixing 1.25% MEKP into the resin and than pouring the resin between two glass plates. The resin was allowed to cure overnight at room temperature than post cured for 5hours at 212°F/100°C.

TESTING METHODS AND RESULTS

Numerous tests were run with literally hundreds of coupons being tested. The scope of this paper allows us to only discuss the results of some of the tests run and to go into detail on only a few of the test results. We will cover those test results that include the factors that had the greatest influence on blister formation.

Two different schedules of exposure can be used to evaluate blistering. One method is to expose each coupon until blisters first start to form on that coupon. The days to first blister formation are recorded. While this method of running the test provides an excellent means of comparing coupons, it does have some drawbacks. This method requires the coupons be removed from the box and checked frequently, which in turn requires the water to be reheated frequently. This method also does not provide coupons that can be used to illustrate a difference between products. The other method is to expose the coupons for a set time period. The coupons are than judged for appearance. While the judging of the coupons is

subjective, we attempted to supply a number value to coupons that would provide a comparison. A score of 100 would be given to a coupon with no blistering. For every percent (rounded to 5%) of the surface that is covered by blisters an equal number of points would be subtracted from 100. A small number of points would be added if the blisters were very small. Additional points will be taken away for large blisters and for fiber wicking. Less than 5 points are adjusted for these factors. This judging system is heavily weighted toward the area covered by blisters and not the type and size of the blister. We found, in our testing, that the size of the blister is influenced the most by gel coat thickness and is also directly related to the area of the coupon being tested.

We started our testing by running gel coated laminates in the 212°F/100°C tester. We began with this test because it is the most common one used in the marine industry and we were already running this test on a regular base. Initially we check the coupons for blisters after 50, 100, and 200 hrs. We found the 100 hrs data gave the best differentiation between the performance of the materials being tested. (Figure #5)

Two sets of coupons, made from the same laminate, were tested. For the third run we made up new laminate formed very well and those that performed poorly in the test had the least amount of deviation in their blister results from test to test. We next ran tests at 150°F/65°C. Initially we checked the coupons for blisters after 250, 500, 1000, and 2000 hrs. (Figure #8) Although the 1000hrs did not give the differentiation we would have liked, going to 2000 hours did not provide much improvement and would have doubled the testing time required. We decided to run our comparison testing at 1000 hrs for the 150°F tests. We ran three test sets with coupons cut from the same laminate that was used for first two tests of 212°F tests. New laminates were fabricated for the coupons used in the fourth and fifth set of tests. Because of length of time needed for these tests and the limited number of spots on the tester, we eliminated some of the products tested after the results of the first set was determined. The results of the five sets of tests were compared. (Figure #9) The deviation for the 150°F tests was less than was seen with the 212°F test. (Figure #10) However the lower deviation may more a function of having less differentiation between the coupons than the test being more repeatable.

Figure #11 is a side by side comparison of the average results for the 212°F and 150°F tests. The high and low ends of the range of products have fairly similar test results. On average the results of the 150°F tests ran 26 points higher than the results of the 212°F test. Some products performed considerably better in the 150°F tests than in the 212°F testing. This better relative performance does not appear to be totally related to the heat deflection temperature (HDT) of the resin. Products "J" and "D" performed much better at 150°F test despite having high HDT values. While it did provide more differentiation between coupons, the 212°F test had a greater test variation. The variation from test to test in the 150°F test, while less than that found in the 212°F tests, was still substantial. Since our desire was to have a test that would have value in comparing the blister resistance of new resins to existing resins that have a history of good blister resistance, we looked at new test methods to reduce the variables in the blister testing.

Our next sets of tests were run at 100°F with 18psi water pressure. We were looking to reduce the temperature to eliminate the effect the resin's HDT might have on blister formation in the higher temperature test. We added the pressure element to accelerate the blistering process. Almost all the coupons were blister free at 1000 hours. The coupons were put back on for 1000 more hours to achieve some degree of differentiation between the resins. Two sets of coupons were tested. The average result of these two sets at 2000 hours is shown in Figure #12. The average deviation for the two sets of test was 2.6. While this test showed good repeatability it was not severe enough to give good differentiation between the VE based resins.

Our desire was to have a test that would have value in comparing the blister resistance of new resins to existing resins that have a history of good blister resistance. We looked at methods that would differentiate between resins, but reduce or eliminate the variables observed in the laminate blister testing. Tests were run with castings without fiberglass made from the same resins used in the previous tests. We ran the tests with and without thixotrope and tested them at 212°F and 150°F. The addition of fumed silica did not significantly effect blistering. The addition of an organo clay did reduce blister resistance.

On the 150°F tester only the orthophthalic and DCPD based resins blistered in fewer than 2000hrs. We discontinued the 150°F tests and focused our effort on the 212°F test. Because of the large difference in time to blister formation, using a set exposure period and comparing amount of blisters on the coupons was not practical for this test. Instead we checked the coupons periodically and recorded the amount of time they were on the box before blister formation along with a score of the degree of blistering. Coupons were removed from the box when the blister score dropped below 50. Two sets of tests were run. Because we used two methods to quantify the blistering, supplying a number to the deviation between the tests is not possible. However, the time to removal of coupons made with the same resin was identical. The blister score varied by an average of 9%. This test does seem to have good reproducibility.

The results of the casting test were compared to the result of the 212°F and 150°F gel coated laminates. (Figure #13) The result of the casting test fell directly inline with expected blister resistance of the resins based on chemistry. The higher the VE content the better the blister resistance. The two VE/PE resins that did poorly in the 212°F gel coated test did as well as the other VE/PE blend in the casting test. Since these products were obtained from the field, we have only general information about them.

When having the similar polymer composition, the higher the styrene in the resin the better the blister resistance. Included in this test was a new modified polyester (MPE) resin. This resin was modified to have some of the same polymer structure as a VE resin with a lower cost. Based on the performance in the casting we would expect it to fall between the VE/PE and the VE modified polyesters. The MPE resin in fact not only performed better than the VE modified polyester, but performed better than some of the VE/PE blends in some of the gel coated laminate blister tests.

Since the gel coated samples did not follow the same relative sequence as the castings, the other components in the laminate must have a significant impact on the blistering. We first looked at the effects of the glass reinforcement on blister formation. We ran a limited number of tests of

coupons made by casting a resin without reinforcement behind the gel coat. The coupons were tested at 212°F. They lasted many times longer on the tester before blistering than did the equivalent laminate. In fact these coupons ran almost as long as the clear castings of the same resin run without the gel coat before blistering.

Because we now knew the glass reinforcement was a major factor in the blister formation, we wanted to determine the influence that the sizing/binder on the fiberglass had on the blister formation. We made a laminate with the DCPD resin "N" using glass mat and another with the same resin using glass mat with the sizing and binder removed. The coupons were exposed for 100hrs on the 212°F tester. The coupon made with the mat had a score of 18. This is similar to the results in the previous testing of gel coated laminates made with this resin. The coupon from the laminate made with the mat with the binder removed had a score of 73. This demonstrates that the sizing/binder on the glass is a significant factor in blister formation.

It is of course impractical to make laminates with fiberglass that has no sizing or binder. However, there is a big difference in the amount and types of binders and sizing used in fiberglass mat and the binder used on the gun roving. To achieve uniform thickness we used fiberglass mat for most of our laminate testing. For our next set of tests we compared laminates made with mat to ones made with gun roving. The same manufacturer made both the mat and the gun roving. These test results demonstrate the large effect the type of sizing and/or binder on the fiberglass has on blister formation.

(Figure #14) The influence of the fiberglass glass on blister formation can be overcome to some degree by using a blister resistant resin. With the general-purpose resin the effect of the fiberglass is very significant.

The effects of gel coat were examined next. To limit the scope of this work we looked at only two different gel coats. The gel coats were drawn down with a 10, 20, and 40 mil draw down bar. Our goal was not to determine all the effects that gel coats have on laminate blistering, but to determine what portion of the blistering difference in

laminates might be attributable to the gel coat. Two sets of coupons from these laminates were run at 212°F for 100 hours and graded. (Figure #15) Because of the variability of the laminate blister testing, we were unable to draw any conclusions as to the degree to which the gel coat affects blistering. However, this test does demonstrate that gel coat thickness and composition has a substantial influence on blister test results. Our tests have also shown that a good skin coat resin cannot compensate for a poor gel coat when good blister resistance is desired.

As an additional test of the influence of gel coat on blistering we ran test of laminates without gel coat. We made some panel with glass cloth backed with glass mat and others with just glass mat. The laminates with the cloth skin coat ran 5-10 times longer before blistering than did the gel coated laminates made with the same resins. Those laminates made with just chopped mat ran about 2-5 times longer than gel coated laminates made with gel coat. Fiber "glinting" was observed well before the formation of blisters. The products high in VE content had much less fiber "glinting" than those products with lower levels of VE. Although we only ran two sets of these tests, we got very similar results in both sets of tests.

CONCLUSIONS

During this testing, over 700 coupons were tested. We are able to present the results of only a fraction of the tests run in this paper. This work by no means answers all the questions about osmotic blistering with composites. Many times as we discovered the answer to one question, two additional questions were created. Blister formation in composites is a complex issue. It is not only influenced greatly by the different components used to make the composite, but also one component may behave differently when used with a different combination of the other components.

Our testing found that many of the tests used to measure blister resistance had very large variability. This variability requires multiple tests be run to have accurate reproducible test results. For the most used test the laminate boil test, a minimum of 3 tests are needed to assure that the results are showing the differences between the components of the laminate and are not just the results of testing variation. Even then, the test can only

show differences between different polymers. Five sets of tests would be needed to have any ability to evaluate resins of similar composition, such as different brands of VE resins.

The 150°F test did provide a greater reproducibility than the 212°F test. However, it required a much longer test period. The time required to differentiate the high performance products could be prohibitive for some product evaluations. The 100°F 18psi test results were similar to those of the 150F ambient tests. Some of the resins with the lower HDT values performed better in the lower temperature tests.

The clear casting test must be run at 212°F to get blister formation in the higher performance products in a reasonable time. The clear casting test appears to be the only test capable of accurately separating resins of similar composition. When testing resins with very good blister resistance, the test had to be run for a very long time before blistering occurred. If one is interested only in which resin is most resistant to blistering the clear casting boil test appears to do the best job.

For the most part, resins that perform well in the casting will do well in gel coated laminates. However, as we have seen, the glass and gel coat used in the laminate can have a large influence on the actual performance of the resin in the laminate. To a great extent the blister resistance of a laminate is determined by the weakest link. Whichever component of the composite has the poorest blister resistance will be the major factor in the blister resistance of the entire composite. One option for evaluating resins is to use the casting 212°F test to compare resins, than use that resin with different gel coat and fiberglass types in a laminate test to determine the optimum combinations of materials.

In our testing we found barrier coats out performed the skin coats for blistering. Based on the contribution of the fiberglass to blister formation, this appears to be a function of having a barrier between the glass fibers and the gel coat.

A majority of the resins with 50% or greater VE resin composition far outperformed the general-purpose resins. Very little difference was seen

between 100% VE products the VE/PE blends that contain 50% VE resin. However, a significant drop off in blister resistance was seen in the resin blends containing less than 30% VE resin.

We demonstrated that a polyester resin could be modified to give it some of the characteristics of a VE resin thereby greatly enhancing blister resistance. The performance of this resin was equal or better than the low VE resin blends currently being used as one-resin systems.

Despite the large number of tests run we have only covered a small portion of the factors that might influence the formation of blisters. This is not a one-time experiment, but rather an ongoing work that will continue indefinitely, as we seek to better understand the factors effecting blister formation in fiberglass composites and how to test them.

Figure 1. Products

VE Barrier Coat	A
100% VE >35% styrene	B
VE Modified PE resin <35% styrene	C
VE/PE <35% styrene	D
VE/PE (Isophthalic) Blend >35% styrene	E
Polyester Modified VE <35% styrene	F
VE/PE Blend <35% styrene	G
PE (Isophthalic) >35% styrene	H
PE (DCPD) >35% styrene	I
VE/PE (Isophthalic) >35%	J
VE Barrier Coat	K
100% VE <35% styrene	L
VE Modified PE resin <35% styrene	M
PE (DCPD) resin <35% styrene	N
PE (Orthophtalic) resin >35% styrene	O
Modified PE <35% styrene	P

Figure 2.



Figure 3.

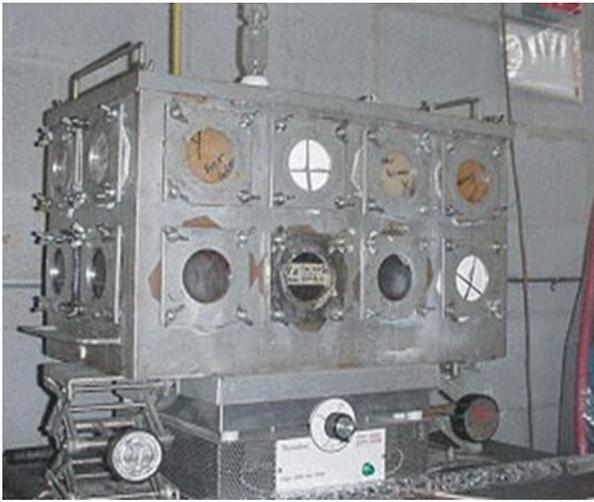


Figure 4.



Figure 5.
First Run 212F

	Hours		
	50	100	200
A	100	99	97
B	96	80	73
C	98	27	23
D	25	9	8
E	99	97	94
F	99	90	36
G	90	28	22
H	90	20	18
I	80	18	6
J	82	20	8
K	98	96	95
L	90	58	8
M	90	19	7
N	75	15	6
O	22	8	6

Figure 6.

Compare runs @ 212F 100 hrs				
CODE	1st	2nd	3rd	Ave
A	99	100	75	91
B	80	95	98	91
C	27	94	30	50
D	9	11		10
E	97	97		97
F	90	92	30	71
G	28	72		50
H	20	80		50
I	18	20		19
J	20	25		23
K	96	95		96
L	58	75	85	73
M	19	40	80	46
N	15	18	10	14
O	8	10		9

Figure 7.

Deviation 212F				
	1st	2nd	3rd	Ave
A	8	9	16	11
B	11	4	7	7
C	23	44	20	29
D	1	1		1
E	0	0		0
F	19	21	41	27
G	22	22		22
H	30	30		30
K	1	1		1
J	3	3		3
L	15	2	12	10
M	27	6	34	22
I	1	1		1
N	1	4	4	3
O	10	1		6
Ave.	11	10	19	12

Figure 8.

First Run 150F				
	250 Hrs	500Hrs	1000Hrs	2000Hrs
A	100	100	100	99
B	100	99	99	99
C	99	99	99	99
D	99	99	99	99
E	99	99	98	97
F	99	99	97	98
G	98	98	98	98
H	98	97	93	90
I	98	97	78	48
J	95	95	90	90
K	95	95	92	90
L	92	92	85	85
M	88	86	80	80
N	88	80	14	10
O	45	10	8	8

Figure 9.

Compare @ 150F1000 hrs						
	1st Fabrication			2nd		AVE
	1st	2nd	3rd	1st	2nd	All
A	100	99	99	100	100	100
B	99	88	95	100	100	96
F	97	88	97	99	98	96
G	98	88	92	80	85	89
H	93	80	95	78	80	85
L	85	48	78	100	100	82
M	80	49	83	99	99	82
N	14	37	42	8	15	23

Figure 10.

Deviation 1000hrs @150F						
	Laminate 1			Laminate 2		AVE
	1st	2nd	3rd	1st	2nd	All
A	0	1	1	0	0	1
B	3	8	1	4	4	4
F	1	8	1	3	2	3
G	9	1	3	9	4	6
H	8	5	10	7	5	8
L	3	34	4	18	18	15
M	2	33	1	17	17	13
N	9	14	19	15	8	14
AVE	4	13	5	9	7	8

Figure 11.
Compare 1000hrs 212F to 100hrs 100F

Product		212	150
VE Barrier Coat	A	91	100
100% VE >35% styrene	B	91	96
VE Modified PE resin <35%styrene	C	50	99
VE/PE <35% styrene	D	10	85
VE/PE(Iso) Blend >35% styrene	E	97	97
Polyester Modified VE < 35% styrene	F	71	96
VE/PE Blend < 35% styrene	G	50	89
PE (Isophthalic) >35% styrene	H	50	85
PE(DCPD) >35% Styrene	I	19	58
VE/PE(Isophthalic) >35%	J	23	89
VE Barrier Coat	K	96	95
100% VE<35% styrene	L	73	82
VE Modified PE resin <35%styrene	M	46	82
PE (DCPD) Resin <35% styrene	N	14	23
PE (Orthophtalic) resin > 35% styrene	O	9	8

Figure 12.
100F at 18psi 2000 hours

Product		
VE Barrier Coat	A	100
100% VE >35% styrene	B	97
VE Modified PE resin <35%styrene	C	99
VE/PE <35% styrene	D	65
VE/PE(Iso) Blend >35% styrene	E	90
Polyester Modified VE < 35% sty.	F	97
VE/PE Blend < 35% styrene	G	99
PE (Isophthalic) >35% styrene	H	95
PE(DCPD) >35% Styrene	I	68
VE/PE(Isophthalic) >35%	J	90
VE Barrier Coat	K	100
100% VE<35% styrene	L	99
VE Modified PE resin <35%styrene	M	98
PE (DCPD) Resin <35% styrene	N	75
PE (Orthophtalic) resin > 35% sty.	O	95