ESTUDIO EXPERIMENTAL SOBRE LA INFLUENCIA DE LOS DEFECTOS DEL PROCESO DE FABRICACIÓN EN LA FORMACIÓN DE AMPOLLAS EN LAMINADOS PROTEGIDOS CON GEL-COAT UTILIZADOS EN AMBIENTES MARINOS

EXPERIMENTAL STUDY ON THE INFLUENCE OF MANUFACTURING PROCESS DEFECTS IN BLISTERING IN GEL-COAT PROTECTED LAMINATES UTILIZED IN MARINE ENVIRONMENTS

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ABSTRACT:

Blisters occur when small quantities of water in form of vapour penetrate a laminate, usually within a marine environment. This reaction generates an internal pressure that causes degradation in Gel-Coating. Then, defects are made evident in the form of blisters. This study looks into the influence of this effect on different manufacturing process defects in gel-coat protected laminates utilized in marine environments

Key Words: Blisters; gel-coat; fibreglass; experimental test; laminates; marine environments; manufacturing process defects

RESUMEN:

Las ampollas se producen cuando pequeñas cantidades de agua en forma de vapor penetran en un laminado, normalmente en un entorno marino. Esta reacción genera una presión interna que provoca la degradación del Gel-Coat. Entonces, los defectos se hacen evidentes en forma de ampollas. Este estudio analiza la influencia de este efecto en diferentes defectos del proceso de fabricación en laminados protegidos con gel-coat utilizados en entornos marinos

Palabras Clave: Ampollas; gel-coat; fibra de vidrio; prueba experimental; laminados; entornos marinos; defectos del proceso de fabricación

1.INTRODUCTION

Blistering is a phenomenon which occurs on some fibreglass reinforced laminates protected with gel coating. Typically, blisters are small bumps on the gel coated surfaces which are continuously exposed to water, with water conditions varying in terms of temperature, pressure or density.

Since blisters are defined as something associated with water exposure, ship hulls are typical applications [1-3] where blisters can be found. These applications are subjected to water exposure, with different pressures on both faces of the laminates [4], different densities of fluids, such as water and water vapour and also different temperatures on both faces [5-6]. These differences may increase the blistering process [7-10,21,22].

Such fibreglass blisters happen when water penetrates the laminate. The laminate is usually protected by a so-called water-proof barrier which is the gel coat. Gel coating has been regarded as a water-proof barrier but in fact it is not such kind of barrier. Gel coating protects against water penetration retarding its penetration. Therefore, the thicker the barrier and the higher the quality of the gel coating, the better the protection the better the application will be.

Blisters are small bumps on the surface of a laminate. These bumps might be just cosmetic defects or might cause delaminating on the lay-up, at least on the layers where blisters are located, regardless of whether these blisters are typically located between the gel coating layer and the adjacent fibreglass layer. The mechanism of blistering is due to an osmosis process which is caused by the diffusion of fluid through a membrane. This process involves the passing of water from a dense liquid into a less dense fluid. Basically it is the tendency for both liquids to mix if their density is different in order to reach osmotic pressure equilibrium.

Once this begins, there is water passing through the laminate at least at molecular level. This water passing through will mix with any other particle or liquid along its path into the other part of the membrane. Along this path, particles of water soluble materials can be found. This is the critical point to be aware of when talking about blistering. Water molecular movement should not be considered dangerous for the laminate, as this process is bound to occur whatever the protection of the laminate or its composition. The problem of that movement lies in the particles which water will join along that path. Those particles which are typically water soluble will join the water in order to form an acid solution which is even capable of corroding polymers. Basically water will react with such components by forming an acid solution which will corrode the laminate.

Those particles likely to be constituents are water soluble particles which do not cure because of it own nature, and some other particles that arise from an incomplete cure of the polymer. Those particles are inhibitors, pigments, promoters, such as octoates, catalyst sizing, emulsions binders, and of course any other impurities which are present in any manufacturing process, such as water vapour dirt, etc.

Three main situations will drive the osmotic process [11-12]:

- Temperature difference between the inner and outer parts of laminate.
- Different pressures on both faces.
- Different density of materials on both faces of the laminate, probably salt water and water vapour in the case of hulls, and water plus chemicals added in order to ensure water ph and microorganism protection, and very likely a very fine water vapour at the supported wall of a swimming pool, in the case of swimming pools.

2. SIMULATION OF DEFECTS ON FIBRE GLASS LAMINATES

The aim of this report is to show the blistering problem in fibreglass laminates. For this purpose, a series of experimental tests have been carried out in a laboratory testing equipment, based in the commercial system named AMOCO “Turtle-box” [13-14].

For these experimental tests, six plates of six different laminates have been produced by means of a spray-gun. The spry-up manufacturing process consists of chopped fibreglass and resin (usually polyester or vynilester) projected on an open mould, by means of a projection gun driven by compressed air, which wets the cut fiberglass with the resin when projected. The layer of resin-impregnated chopped glass fibre strands is usually compacted by means of grooved rollers, in order to obtain a compact product. The cycle is repeated as far as the laminate is obtained. Direction of projection is usually changed 90º in order to produce an isotropic laminate due to fibre orientation. The air must be dry, and the supply of glass and resin must be well regulated. It is convenient to have a suction hood to keep atmosphere clean and safe during the projection because of solvents. Resin was projected at 4kPa and fiberglass chopper was set at 7 kPa on a Binks spray gun. Parameters of laminates are shown in table 1.

All panels where manufactured at Vetrotex facilities in Alcalá de Henares (Spain).

These laminates are based on the p292s fibreglass roving. The Laminate 1 was used as reference model and it was compound of two layers. These layers are a gel-coat and a protection barrier. The five remaining laminates (Laminates 2 - 6) are compound of four layers. These layers are the following

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- A gel-coat layer
- A protecting barrier layer
- A sprayed fibreglass layer
- A sprayed fibreglass plus CaCO3 layer

The six types of laminates produced and the layers of each of them are shown in Table 1.

Layers	*Laminate 1* *Reference*	*Laminate 2* *Normal Processing*	*Laminate 3* *Wet fibreglass*	*Laminate 4* *Low Gelcoat thickness*	*Laminate 5* *Dispersed excess of catalyst*	*Laminate 6* *No rolling after spraying 3rd layer*
1st layer Gel-coat	0.65 mm Gel Coat NP6	0.65 mm Gel Coat NP6	0.65 mm Gel Coat NP6	0.40 mm Gel Coat NP6	0.65 mm Gel Coat NP6.	0.65 mm Gel Coat NP6.
2nd layer Barrier	0.25mm Vinyl-ester resin	0.25 mm Vinyl-ester resin	0,25 mm Vinyl-ester resin	0.25 mm Vinyl-ester resin	0.25 mm Vinyl-ester resin + Catalyst drops	0.25 mm Vinyl-ester resin
3rd layer Resin + Fibre		Orthopthalic Estratil 2170L	Orthopthalic Estratil 2170L	Orthopthalic Estratil 2170L	Orthopthalic Estratil 2170L	Orthopthalic Estratil 2170L
		P292S 16 mm. cut ± 30%	P292S 16 mm cut± 30%	P292S 16 mm cut ± 30%	P292S 16 mm cut ± 30%	P292S 16 mm cut ± 30% Non rolled layer
4th layer Resin + Fibre		Orthopthalic plus (CaCO3)	Orthopthalic plus (CaCO3)	Orthopthalic plus (CaCO3)	Orthopthalic plus (CaCO3)	Orthopthalic plus (CaCO3)
		P292S 16 mm cut ± 25%	P292S WET 16 mm cut ± 25%	P292S 16 mm cut ± 25%	P292S 16 mm cut ± 25%	P292S 16 mm cut ± 25%

Table 1. Layers of the laminates produced

In order to obtain the blistering problems [15-16], four of the six laminates manufactured were produced with common defect in the manufacturing process of fiberglass laminates [17-22].

In particular, in the manufacturing process of the Laminates 3, the fiberglass used was wet. Wet fiberglass was achieved by means of sprayed water in roving bags. Humidity was measured according to EN 334. Humidity was kept between 1.2% and 1.5%. The Laminates 4 have been produced with a thickness of the gel coat layer lower than the necessary. In the Laminates 5, the amount of catalyst employed in production of the specimen exceeds in a 15% the recommended quantity. The Laminates 6 were manufactured with a defect of bad compaction process.

Wet fibers in the manufacturing process (Laminate 3) are a real problem due to the humidity introduced into the laminate. Once the laminate begins to cure, the humidity turns into water which will be able to flow through laminate. This water would cause blisters in the laminates

A thickness of gel-coat lower than the necessary (Laminate 4) would produce a laminate with a weak protected. Gel-coat layer protects to laminates of external water and blocks flows of water through the laminates. If laminate thickness is not enough, water could penetrate into the laminate and once there, produce blisters.

An excess of catalyst (Laminate 5) is a major problem. This defect generates a fast polymerization reaction and a higher temperature on the laminates which could lead to cracks of the same.

Defect of bad compaction process (Laminate 6) leads to excess of resin, water, air, which originates internal cracks. Water can flow through this cracks and it would cause blisters in the laminate

3. EXPERIMENTAL TEST OF BLISTERING

Normally blisters do not show up when recently get in service. The osmotic mechanism of the blisters need some years in service to show up. Besides it has been observed that warmer seas or warmer water produce an increase in blisters on the hull of boats.

For these reasons the experimental test carried out is an artificial aging of several laminates, which reproduce the effect of several years of service of these components.

3.1 LABORATORY TESTING EQUIPMENT

The experimental tests have been carried out in a laboratory testing equipment, produced by the Mechanical Department of the University of Zaragoza, based in the commercial system named “Turtle box” of the AMOCO Company.

Fig. 1. Laboratory testing equipment

The laboratory testing equipment made for this study has a cube shape. The four lateral faces and the bottom face of the equipment were manufactured in rust-proof stainless steel and subsequently these sheets were joined by welding. The thickness of these sheets is 2mm. In the lateral faces have been mechanized nine holes. The top section of the equipment is closed by another plate. This plate was designed with a hole in the centre thereof. The purpose of this hole is to allow input a resistor and a stirrer in the equipment, as well as refill the equipment with water when it´s necessary. In addition, the laboratory testing equipment is equipped with a thermostat which allows to control the water temperature in the equipment. Figure 2 shows the thermostat located into the turtle box. It is located somehow in a representative location in order to get mean temperature measures.

Figure 3 shows the stirrer setup. Stirrer was placed in order to ensure a mean temperature all over the turtle box. Stirrer was permanently connected stirring up the water. Also setup of resistance is shown. Resistance was a 9KW rig connected to the thermostat. Such rig performed quite well and temperature achieved was constant during the testing.

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Fig. 2. Location of the thermostat

Fig. 3. Location of the stirrer and the resistance in the box

3.2 DESCRIPTION OF THE EXPERIMENTAL TEST

In order to carry out the experimental test, the produced samples must be coupled to the laboratory testing equipment.

Samples where all cut out from manufactured panels of 1.5mx1.5 m. Samples were cut off by means of diamond blade saw. Coupons were cut off in order to match a 14x140 mm square which fits perfectly de holes of the turtle box.

Thus each of the 36 produced samples was placed in one of the 36 holes on the sidewalls of the laboratory testing equipment. These samples were placed in the equipment with the gel coat layer inwards and were attached to the laboratory testing equipment with washers. These washers were of non-rustproof steel, and were attached to the equipment by means of two screws. In order to obtain a watertight seals, a natural rubber gasket was placed between the samples and the sidewalls of the equipment. The attachment system of the panels is shown in figures 1 and 4. Also Figure 2 shows the gel coat part of the laminate exposed to water.

The distribution of the 36 samples was made in 12 vertical columns of 3 panels. Each sidewall of the equipment had 3 vertical columns. The six samples of each laminate type were been placed in two columns. An example of this distribution is shown in figure 4.

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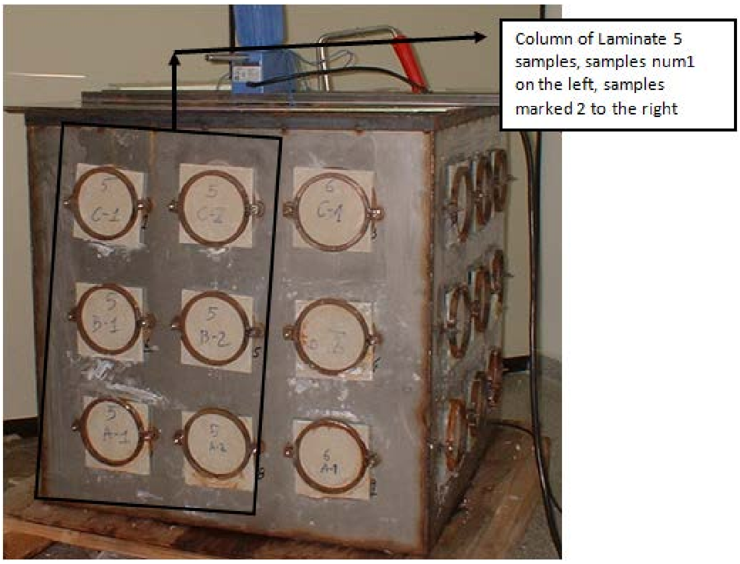

Fig. 4. Distribution of the six samples of the Laminate 5 in the equipment

Once all the panels were attached to the equipment, the laboratory testing equipment was filled with water. This water was heated up to 65ºC by the resistor placed inside it. In order to ensure a constant temperature of the water, a stirrer was permanently functioning inside the equipment. In addition, the resistor was connected to a thermostat. This thermostat turns on or turns off the resistor if the water temperature was arising or below to 65º.

During the test, water levels and temperature levels were checked on a daily basis.

As mentioned beforehand, blisters do not appear at the commissioning of the ship. Normally some years of service are required to this effect appears. For this reason, the experimental test developed reproduces the effects of 1, 2 and 3 years of actual sailing.

To carry out the test, the manufactured panels were divided into three groups, named A, B and C. The group named A was composed by the 12 panels located in the lower line of the laboratory testing equipment. The group B are composed by the 12 panels located in the middle line of the laboratory testing equipment. And the group C are composed by the 12 panels located in the upper line of the laboratory testing equipment. With this arrangement each group is formed by two samples of each of the six laminates produced.

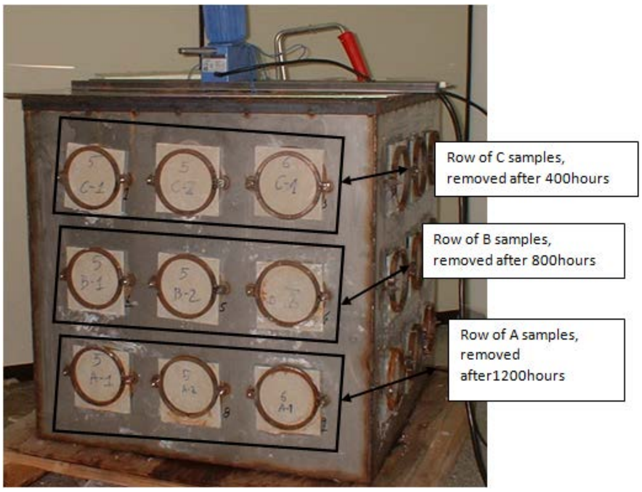

Fig. 5. Distribution of samples. Horizontally placed group (A, B, C)

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The difference between the three groups of samples in the test (A, B and C) corresponds to the time of exposure to the hot water on the laboratory testing equipment of the samples. Specifically, the time of exposure was 1200, 800 and 400 hours for the groups A, B and C respectively, as shown in Fig 5.

3.3 REALIZATION OF THE EXPERIMENTAL TEST

Once the samples had been placed in the laboratory testing equipment and this had been filled with water at 65ºC, the experimental test was started.

The first phase of the experimental test was completed after the first 400 hours. This time of exposure corresponds to a one year of actual sailing. In this moment, the water that covered the specimens in the upper line of the equipment (group C) is extracted, but keeping the water that cover the specimens of the groups A and B. Once the water of the upper of the laboratory testing equipment has been removed, the test was finished for the samples of the group C, and these samples were disassembled. Meanwhile, the experimental test continues for the groups A and B.

The second phase of the experimental test was completed after 800 hours. This time of exposure corresponds to a two years of actual sailing. In this moment, the water that covered the specimens in the middle line of the equipment (group B) is extracted, but keeping the water that covers the specimens of the group A. Once the water of the upper of the laboratory testing equipment has been removed, the test was finished for the samples of the group B, and these samples were disassembled. Meanwhile, the experimental test continues for the group A.

The experimental test was finished after 1200 hours. This time of exposure corresponds to a three years of actual sailing. In this moment, the water remaining in the apparatus was emptied, and the samples of the group A were disassembled.

Testing could be easily repeated if necessary in the same way due to the extremely simply setup and conditions .

4. RESULTS

All samples disassembled at the end of every phase have been examined and photographed in order to assess the presence of blisters on the gel coat surface and the reverse surface. The main results obtained of this examination are shown in the following points.

4.1 GROUP C – SAMPLES SUBMERGED 400 HOURS AT 65ºC

Once the samples of the upper line of the laboratory testing equipment (group C) were disassembled, all of them were examined and photographed in order to assess the presence of blisters on the gel coat surface and the reverse surface. The analysis of the samples and the photographs of the group C samples show that no blisters were found on the exposed surface of all samples. These results are summarized in Table 2.

Samples	*Laminate 1*	*Laminate 2*	*Laminate 3*	*Laminate 4*	*Laminate 5*	*Laminate 6*
C1	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters
C2	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters

Table 2. Results of samples submerged 400 hours (Group C)

4.2 GROUP B – SAMPLES SUBMERGED 800 HOURS AT 65ºC

Once the second phase of the test was finished, group B samples were disassembled, examined and photographed. The analysis of the samples and the photographs of these samples show that no blisters were found on the exposed surface of all samples. These results are summarized in Table 3.

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Samples	*Laminate 1*	*Laminate 2*	*Laminate 3*	*Laminate 4*	*Laminate 5*	*Laminate 6*
B1	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters
B2	No blisters	No blisters	No blisters	No blisters	No blisters	No blisters

Table 3. Results of samples submerged 800 hours (Group B)

4.3 Group A – Samples submerged 1200 hours at 65ºC

After a period of 1200 hours, the experimental test was finished. At this moment group A samples were disassembled, examined and photographed. The results of the examination of these samples show that in samples of laminate 2 (normal processing) not appears blisters on the tested surface under the tested conditions, as well as in samples of laminate 3 (wet fibre) and samples of laminate 6 (no rolling after 3rd layer). Blisters are found in samples with an excess of catalyst (Laminate 5) as well as in samples with a low gel coating thickness (Laminate 4). There is a significant difference between blistering effect in the samples of laminate 4 and laminate 5. For samples of laminate 4, small blisters in a very small area have been identified, as shown in table 4 and Fig 6. This results show that blisters may appear in thin gel coat layers, but these blisters are not massive. On the other hand, samples with an excess of catalyst show massive blisters. Sample A-1 of Laminate 5 shows a great area with blisters, as shown in Figure 7.

Samples	*Laminate 1*	*Laminate 2*	*Laminate 3*	*Laminate 4*	*Laminate 5*	*Laminate 6*
A1	No blisters	No blisters	No blisters	Blisters	Blisters	No blisters
A2	No blisters	No blisters	No blisters	Blisters	Blisters	No blisters

Table 4. Results of samples submerged 1200 hours (Group A)

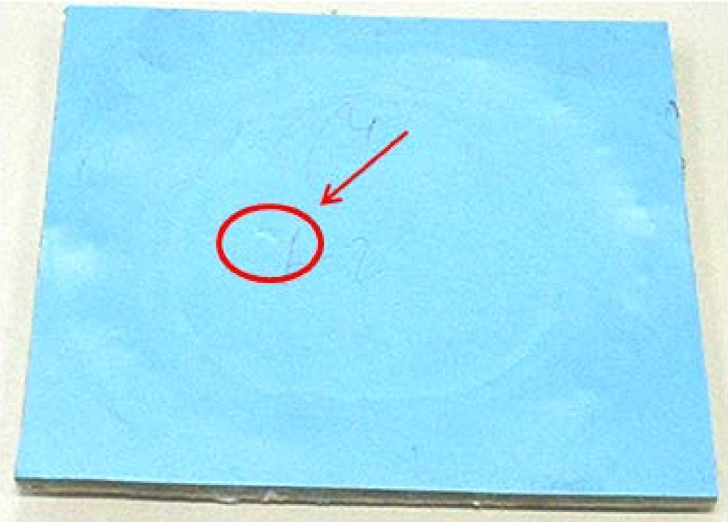

Fig. 6. Blister on the exposed to water surface in the sample A-2 of the Laminate 4

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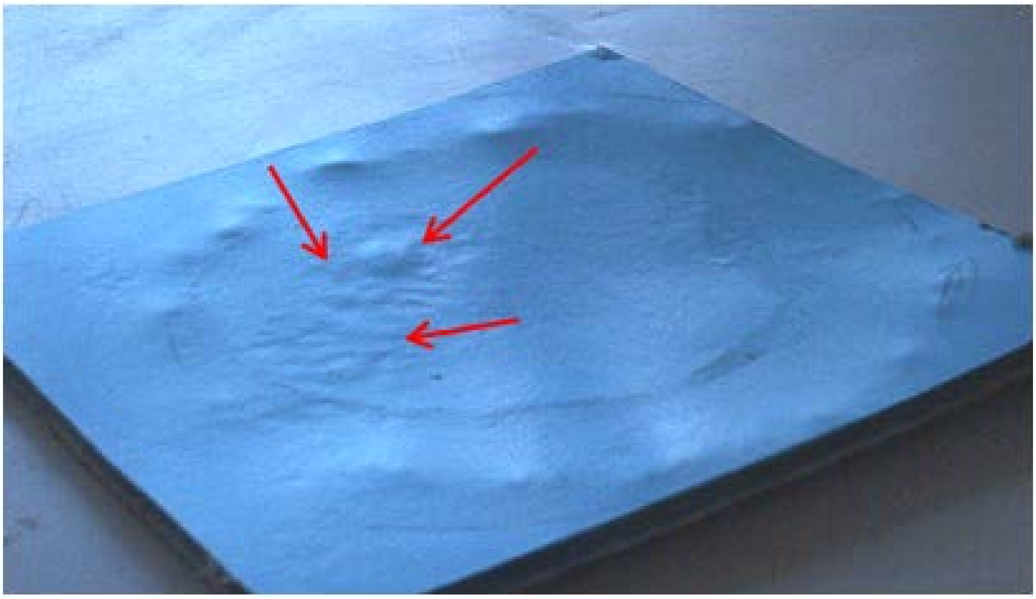

Fig. 7. Massive blisters on the exposed to water surface in the sample A-1 of the Laminate 5

4. ADDITIONAL RESULTS

All An unexpected effect occurred in this test. As it has been explained in advance, the surface exposed to the 65ºC water box showed no blisters for any sample on Laminates 2, 3 and 6, and some for Laminate 4 and 5. Regardless of that result, blisters have been detected in laminates of some samples in the side that never entered into contact with the hot water.

These blisters affect all samples with corroded washers. Besides, these blisters increase in both number and area depending on the type of Laminate. In Laminates 4 and 5 with the same corrosion on washer, blisters were greater and were showed in greater amount than in Laminates 2, 3 or 6 for the same amount of corrosion on washer. This is not a quantitative conclusion as much as a rather qualitative appreciation. Fig 8 shows this phenomena.

These results indicate that blistering phenomena in gel-coat protected laminates are not only produced in the side in contact with the water. In the side without contact with the water, the blistering phenomena are generated by the corrosion on washers.

Sample		Test num 2		Test num 3		Test num 4		Test num 5		Test num 6	
Type	num	Blister	oxi.	Blister	oxi.	Blister	oxi.	Blister	oxi.	Blister	oxi.
C	1	1	1	2	1	1	1	2	1	2	1
	2	1	1	1	1	1	1	2	1	2	3
B	1	2	5	2	5	2	2	2	2	1	2
	2	1	2	2	1	1	1	1	2	2	3
A	1	3	5	2	4	2	1	3	3	2	4
	2	2	4	1	1	1	1	3	2	3	3

Level	1	2	3	4	5
	very low	low	middle	high	very high

Table 5. Results. Comparison and relation of blisters and oxidation

Level is based on both number and size of blisters. Being size and areas different it not possible to attempt to state a quantitative classification.

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Fig. 8. Test num. 2, massive blisters on slightly corroded areas, and massive blisters on highly corroded areas

5. CONCLUSIONS

The main objective of this project is to analyse the blistering phenomena in gel-coat protected laminates generated by actual sailing and manufacturing issues.

In order to fulfil this objective, an experimental test has been carried out. This test reproduces the effect of one, two and three years of actual sailing.

In the manufacture of the samples have been distinguished 6 groups. Four of these groups were produced with common defects in the manufacturing process of fibreglass laminates.

In the samples of laminate 2 (normal processing), laminate 3 (wet fibre) and laminate 6 (no rolling after 3rd layer) there are no blisters on the tested surface under the tested conditions. These results are fully consistent and compares to those shown in [15, 17]

Blisters are found in samples with an excess of catalyst (Laminate 5) and as well in samples with a low gel coating thickness (Laminate 4). Specifically, samples with an excess of catalyst show massive blisters.

In the examination of the tested samples have been detected blisters on the surface not exposed to hot water. These blisters were due to the corrosion of the washers. The samples with greater corrosion of the washers are the samples with greater blisters. This

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effect is greater in samples of laminates with an excess of catalyst (Laminate 4), as well as in samples with low gel coating thickness (Laminate 5).

Main findings in this article can be summarised as follows:

- After 2400h at 65ºC (3-5 years service) test laminates with no manufacturing severe problems such no rolling or slightly wet fibre are ok.
- No matter a Vinyl-ester protecting coating is enclosed, excess of catalyst or low gelcoat thickness will lead to blisters in a relative shot time. A short period could be stated as a 3-5 year of marine or aquatic service.
- Non stainless fasteners corroded could lead to a very rapid blister development in such area.

DATA AVAILABILITY

Authors can confirm that all relevant data are included in the article, further data are available on request.

REFERENCES

[1] Hugo du Plessis. “Fiberglass Boats: Construction, Gel Coat, Stressing, Blistering, Repair, Maintenance”. Published by Adlard Coles Nautical. London. 2010.

[2] Krstulovic-Opara L, Domazet Z, Garafulic E. “Detection of osmotic damages in GRP boat hulls”. Infrared Physics &Technology, Vol 60, pp 359-364. 2013

[3] Marsh G. “Fighting off the blisters”. Reinforced Plastics, Vol 47, pp 39-43. 2003

[4] Rhee KY, Lee SM, Park SJ. “Effect of hydrostatic pressure on the technical behavior of sea water-absorbed carbon/epoxy composite”. Mater Sci Eng A, vol. 384, p.308-313, 2003

[5] Aktas A, Uzun I. “Effect of water absorption on the mechanical properties of glass/polyester composites”. Materials Design, Vol 28, pp 1647-50, 2007

[6] Nigel Clegg. “A short Guide to Osmosis and its Treatment” Published by Nigel Clegg Associates. Sedgefield (UK), 2009

[7] Arun K.V, Basavarajappa S. Sherigara B.S. “Damage characterization of glass/textile fabric polymer hybrid composite in sea water environment”, Materials and Design, Vol 31, pp 930-939, 2010

[8] Kokarakis J, Taylor R. “Theoretical and experimental investigation of blistered fiberglass”. Proceedings of the Third International Conference on Marine Applications of Composite Materials. Melbourne (Fl): Florida Institute of technology. March 1990

[9] Birley A.W, Chen F. “Blistering of GRP laminates in water: 2. Further study of the factors affecting blisters formation” Plastics, Rubber and Composites Processing and applications. Vol 15, nº3 pp 169-176. 1991

[10] Hartoft P., Browning G. “Fiberglass Blisters. Explanation, Diagnosis and Repair” Published by Hartoft Marine Survey, LTD. 1995

[11] Davis R. Ghota J.S, Malhi T.R, Pritchard G. “Blister formation in Rp:The origin of the osmotic process” Proceeding s of the 38th Annual Conference, Reinforced Plastics/Composite Institute, Houston, Texas, USA. Feb 1983.

[12] Ghota J.S, Pritchard G. “Osmosis in resins and laminates” Developments in reinforced plastics. Vol 3 pp 63-95. London. 1984.

[13] Ken Tsuzuki E, Taniguchi C. “Gelcoat Blistering and the use of Glassflakes” Proceedings of the Twelfth International Offshore and Polar Engineering Conference. Kitakyushu, Japan. May 2002.

[14] Cuartero J, Lacamara O, Miravete A, Alonso A, Castejon L. “Ensayo AMOCO de “blistering” sobre laminados protegidos con gelcoat”. Proceedings of the V Congreso Nacional de Materiales Compuestos (Spain). July 2003

[15] Adams, R. C. "Variables Influencing the Blister Resistance of Marine Laminates," 37th Annual Conference, SPI Reinforced Plastics/Composite Institute. Advanced Materials, Manufacturing and Testing Information Analysis Center (AMMTIAC). January 1982

[16] Herzog D.J, Burrell P.P.”An update on the study of permeation barriers to prevent blisters in marine composites and a novel technique for evaluating blisters formation” Proceedings of the 2nd Biennial International Composites Africa. Johannesburg, South Africa 2004

[17] Rockett T.J., Ph.D. and Rose V., Ph.D. 1989. “The causes of boat hull blisters” Department of Chemical Engineering; University of Rhode Island; Kingston, Report for US Coast Guard Grant # 1501, 83, 1987

[18] Antonio Miravete et als. “Materiales Compuestos” Publised by Antonio Miravete. Zaragoza (Spain). 2000

[19] Pablo Antequera, Lorenzo Jimenez, Antonio Miravete, JoséUllod. “Proceso de transformación de la fibra de vidrio” Publised by Vetrotex España. Spain. 1994

[20] Landowski M, Budzik M, Imielinska K. “Degradation of Gel-Coat Layer in Glass/Polyester Laminate in Seawater Environment” Solid State Phenomena, Vol 183, pp 107-110. 2012

[21] P Castaing, L Lemoine, A Gourdenneb. “Mechanical modelling of blisters on coated laminates I - theoretical aspects” Composite Structures 30 (1995) 217-222

[22] P Castaing, L Lemoine, A Gourdenneb. “Mechanical modelling of blisters on coated laminates II – experimental analysis” Composite Structures 30 (1995) 217-222

[23] Amr A Abd-Elhady, A Meroufel, H El-Din M Sallam and M Atta. “Experimental and numerical determination of critical osmotic blister size affecting the strength of aged FRP seawater pipe” Polymers and Polymer Composites 1–14 DOI: 10.1177/0967391120922397. 2020

[24] Magnus Burman1 , Fredrik Stig and Dan Zenkert. “Blister propagation in sandwich panels” Journal of Sandwich Structures & Materials. DOI: 10.1177/1099636219838038. 2019