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**BOAT HULL BLISTERS: REPAIR TECHNIQUES
AND LONG TERM EFFECTS ON
HULL DEGRADATION**

FINAL REPORT

Submitted to

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16. Abstract Abstract of "Boat Hull Blisters: Repair Techniques and Long Term Effects on Hull Degradation" The report documents the research and experimental work undertaken to further explore the causes and nature of osmotic blisters, experiments performed in techniques to reduce the formation of the blisters and repair of damage caused by the formation of blisters. The work is contained in the following sections: Introduction; Causes and Nature of Boat Hull Blisters; Water Solubles - Air Inhibition Studies; Water Solubles Associated with Glass Reinforcements; Swelling Stresses Produced by Diffusion; Long Term Damage by Water Absorption; Effects of Gel Coat on Leaching of Water Soluble Material from Laminates; The X-Layer, a Diffusional Interphase; Blister Initiation Time Distribution; Blistering of Shop Prepared Samples; Effect of Coatings on Water Diffusion Profiles; Drying of Hull Materials During Repair; Types of Repair Coatings Investigated; Performance of Repair Coatings; Evaluation of Repair Techniques; Recommendations for Repair of Blistered Boats; Summary of Conclusion; References. <i>Keywords: Hulls; FRP (Filament Reinforced Plastic); (KT) ←</i> <i>Marine</i>					
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1. INTRODUCTION

The blistering of boat hulls is a serious problem which affects many fiber-glass polyester boats. It can range from a surficial cosmetic problem to a deep-seated structural condition which can threaten the sea-worthiness of a boat. It is costly to the boat owner and is a threat to the competitiveness of the American boat building industry. From this report and other recent studies, a thorough understanding of the causes of the problem has been reached. If a boat hull is susceptible to the problem, once blistering starts, certain corrective actions must be taken or the problem will worsen and become more deep-seated. The second part of this report focuses on the repair and prevention of blistering. As materials change due to development and regulations, new experimentation must continue to ensure that blister resistance is maintained in new boats.

This report discusses the research conducted at the University of Rhode Island for the American Boat Builders and Repairers Association under the direction of Mr. Thomas Hale. The work was funded by the United States Coast Guard and was monitored by Mr. Donald Ellison of the Office of Boating Safety. The research was conducted from September 1986 to August 1988.

2. The Causes and Nature of Boat Hull Blisters

There are a number of types of blisters that can occur in FRP boats. These include osmotic blisters, gas blisters, paint blisters and catalyst blisters. In this research, we are concerned with osmotic blisters.

Three conditions are required for the formation of osmotic blisters--water, water soluble material and a semi-permeable membrane. Even in well mixed and well made composites, blisters may occur through the following sequence of events. All polymers can hold within their structure a certain number of water molecules. Polyesters, the most common polymer matrix for fiber glass boats, typically can hold 0.6 to 2 weight percent of water at saturation, i.e. the point at which all water sites are filled. If a piece of dry new polyester is placed

in water, the water molecules will, by jumping from site to site (diffusion), enter the structure. This will continue until all water sites are full and this will take a considerable time. The material is now saturated. The time necessary for saturation depends on temperature, the exact type and curing schedule of the polyester and the type and amount of glass and filler in the polymer. The section on water diffusion profiles in this report shows how and when saturation is reached at each point in a boat hull. The surface in contact with water saturates first.

As saturation is approached, clusters of water molecules form tiny water droplets. There are micro-stresses within the polymer caused by polymerization shrinkage (the process that converts the liquid resin to a solid polymer) and by slight swelling of the polymer as the water sites fill. These stresses act on the water clusters to change their shape from round droplets to disk shaped clusters (see section five). At this point, no damage of any kind has taken place.

For blistering to occur, these water clusters must dissolve something from the polymer chains or dissolve a water soluble component that is inside the polymer that may have been incorporated during the manufacture of the boat hull. Water soluble species are discussed in sections three and four of this report. The harmless water cluster, which can only form at saturation, has now become a solution.

One of the basic laws of chemical equilibrium requires that two solutions, separated by a permeable membrane, will try to reach the same concentration. The cluster solution is more concentrated than the outside solution (sea water or lake water). To become equal in concentration, the internal droplet will draw in water through the polymer from the outside water. This will cause the cluster to grow into a droplet and as it does, it will exert a swelling or osmotic stress on the surrounding polymer. This force will grow until it is great enough to crack the polyester. Since the cluster was already in a disk shape the cracking will take the form of a solution filled disk-shaped crack. These internal disk cracks (or penny-shaped cracks) are the beginning of a blister. The crack will

cease growing when the internal swelling or osmotic pressure is relieved. However, the increased amount of solution can now react with more polymer or water soluble constituent in the water because of the increased surface area between the polymer and the solution. The reaction increases the concentration of the solution, which in turn causes more water to enter the disk crack. This causes a new pressure build-up in the disk crack and eventually more cracking.

The pressure in the growing disk crack eventually causes solution filled cracks to open which are from 1/4" to 1" or 2" in diameter. As these large cracks open in the hull they follow the path of least resistance. Since the reinforcing fiberglass in the hull lies parallel to the surface, the crack will open between the layers of fiberglass and grow from the nucleating disk crack outward, parallel to the gel coat surface. If the growing circular crack filled with pressurized solution is near the surface, the overlying gel coat and resin will bulge outward forming the typical surface blisters seen on boats. Sometimes the pressure is great enough so that the overlying cap breaks open. If a boat is removed from the water and a blister is punctured, a stream of acidic smelling solution can squirt many feet.

As water saturation progresses deeper into the hull, the above mechanism will take place at deeper levels. When the cracks begin to open at a deep level, particularly in heavily reinforced woven roving zones, the laminate is so resistant to bulging that the solution pressure can only be relieved by forming deep osmotic cracks that can lead to delamination of the hull. Section 6 discusses this type of damage.

On reflection, it becomes obvious that the blistering process can be stopped at several junctures. Water cannot be kept out of the hull (except by metal cladding), but the water level can be kept below saturation by good maintenance and by keeping the bilge side reasonably dry. In section nine, water diffusion profiles are discussed and the importance of bilge side water pick-up is emphasized. A second method for preventing blister formation is to eliminate or minimize the water soluble components in the resin and on the glass. Much has been made of the greater hydrolytic stability of isophthalic resins as

compared to orthophthalic resins, but the added water resistance of the resin itself is meaningless if other water soluble components are introduced during production. The final method, which is least practical, would involve the development of a polymer which would be so strong that it could resist osmotic cracking even in the presence of cluster solutions.

If a hull blisters, it should be repaired before the damage becomes deep and structural. The second part of this report describes experiments and makes recommendations, for the repair of blistered boat hulls. A shorter version of this report which contains only the repair recommendations is available from the American Boat Builders and Repairers Association, 715 Boylston St., Boston, MA 02116.

3. Water Solubles - Air Inhibition Studies

Since water soluble materials in the resin are necessary for blister formation and since air inhibition will create a water soluble component, several experiments were conducted to determine ways to reduce this effect. An air inhibition layer is a sticky tacky layer that forms on a gel coat surface, during cure, when exposed to air. This layer is water soluble. It forms by the reaction of oxygen with any free radical in the system. It is usually caused by the reaction with styrene.

A set of samples was constructed and tested to help evaluate the effect the air inhibition layer has on blistering. The study focused on the method of elimination of the layer as well as and method of removal of the air inhibition layer.

Seven different procedures were tested. These were:

1. Wax paper was placed over the gel coat, in the wet state, right after draw down and removed just prior to laminating.

2. Various types of peel ply were placed over the gel coat, in the wet state, after draw down and removed just prior to laminating.

The types of peel ply tested were:

- a) Plastic
 - b) Coarse nylon cloth
 - c) Fine nylon cloth
 - d) Coarse polyester cloth
3. The air inhibition layer was washed off with acetone and the gel coat was dried for one hour before laminating.
4. The air inhibition layer was washed off with styrene and the gel coat was dried for one hour.
5. The air inhibition layer was sanded off prior to laminating.
6. The air inhibition layer was removed with a scraper prior to laminating
7. The air inhibition layer was not removed.

All laminates were constructed by drawing down a 20 mil gel coat onto a 12" X 12" waxed glass mold. Orthophthalic Acid/Neopentyl glycol based gel coat was used in the R, RA, RB and RD series. Isophthalic acid/Neopentyl glycol based gel coat was used in series RC. Two to 2.5% MEKP was used for curing. The samples were divided into four or five sections and one of the procedures, listed above, was performed on each section of the laminate. The glass reinforcement and laminating resin were then rolled on. Four layers of glass reinforcement were used; one layer of veil mat and three layers of woven roving. Orthophthalic acid based laminating resins were used in the R, RA, RB and RD series and isophthalic acid based resin in series RC. Two percent MEKP was used in all cases. The samples were allowed to cure approximately two weeks and until constant Barcol hardness readings were obtained for the front and backside of the laminate. All samples were tested at 65°C by single sided exposure. The samples were checked periodically for blister initiation time and severity. Results are given in Table 1.

From this study it was found that placing a sheet of wax paper on top of a wet gel coat, once drawn down, prevents the air inhibition layer from forming. The gel coat surface was hard and not sticky. Samples prepared using this

Table 1. Blister Initiation Time and Blister Density for Samples with Controlled Air Inhibition Layers. After One Month at 65°C

Ser- ies	Sam- ple No.	Del coat type	SWEP	Procedure	Time of Procedure after Drw down (hrs)	Time of Laminating after drw down (hrs)	Laminates type	SWEP	Blister initiation time (hrs)	Blister density (blister/cm ²)	Max blister size (cm ²)	Dis- colora- tion
R	1	ortho/MPG	2.5	1	0	2.0	ortho	2.0	31±14	6.3	0.5	0
R	2	ortho/MPG	2.5	3	1.0	2.0	ortho	2.0	31±14	4.6	1.0	0
R	3	ortho/MPG	2.5	5	2.0	2.0	ortho	2.0	31±14	3.9	1.2	3
R	4	ortho/MPG	2.5	7	---	2.0	ortho	2.0	31±14	5.6	0.5	4
RA	1	ortho/MPG	2.5	1	0.25	2.0	ortho	2.0	180±12	2 trg 10 mm blisters	1.0	1
RA	2	ortho/MPG	2.5	3	1.0	2.0	ortho	2.0	105±15	3.2	0.5	1
RA	3A	ortho/MPG	2.5	5	2.0	2.0	ortho	2.0	64±26	5.1	0.3	3
RA	3B	ortho/MPG	2.5	6	2.0	2.0	ortho	2.0	46±26	6.4	0.5	3
RA	4	ortho/MPG	2.5	7	---	2.0	ortho	2.0	132±12	3.8	.03	4
RB	1	ortho/MPG	2.5	1	1.0	20.0	ortho	2.0	227±12	33 blisters	0.7	2
RB	2	ortho/MPG	2.5	3	19.0	20.0	ortho	2.0	64±12	5.2	0.6	1
RB	3a	ortho/MPG	2.5	5	20.0	20.0	ortho	2.0	132±36	2.5	0.3	3
RB	3b	ortho/MPG	2.5	6	20.0	20.0	ortho	2.0	227±12	2.6	0.5	3
RB	4	ortho/MPG	2.5	7	---	20.0	ortho	2.0	398±12	4.0	0.2	6
RC	1	ISO/MPG	2.0	4	1.0	2.0	ISO	2.0	64±12	7.3	0.1	2
RC	2	ISO/MPG	2.0	3	1.0	2.0	ISO	2.0	64±12	7.3	0.6	2
RC	3a	ISO/MPG	2.0	5	2.0	2.0	ISO	2.0	146±72	4.2	0.2	3
RC	3b	ISO/MPG	2.0	6	2.0	2.0	ISO	2.0	146±72	4.6	0.1	3
RC	4	ISO/MPG	2.0	7	---	2.0	ISO	2.0	146±72	2.2	0.1	2
RD	A	ortho/MPG	2.0	2A	0	1.0	ortho	2.0	130±34	0.4	0.2	-
RD	B	ortho/MPG	2.0	2B	0	1.0	ortho	2.0	130±34	0.6	0.3	-
RD	C	ortho/MPG	2.0	2C	0	1.0	ortho	2.0	130±34	2.2	0.3	-
RD	D	ortho/MPG	2.0	2D	0	1.0	ortho	2.0	130±34	1.5	0.3	-
RD	F	ortho/MPG	2.0	7	---	1.0	ortho	2.0	130±34	1.0	0.6	-

KEY:

Procedure (abbrev. #) Discoloration

- 1 Wax Paper 0 - none
- 2 Peel ply. 1 - slight (spotty)
- 3 Acetone wash 2 - slight (uniform)
- 4 Styrene wash 3 - severe (spotty)
- 5 Sanding 4 - severe (uniform)
- 6 Scraping
- 7 no treatment
- * see text for details

procedure performed best. Generally, few large blisters, as well as some smaller ones, formed and the gel coat was only slightly discolored.

Use of the wax paper in the Rb series did not perform as well as it did in the R and RA series. However, it still performed better than any of the other procedures in that series. The reason for this is that the wax paper was placed one hour after draw down of the gel coat. A significant amount of air inhibition formed within an hour.

Removal of the air inhibition layer with acetone appeared to be the second best procedure. Blisters tended to be concentrated in regions. These regions could have been areas where the air inhibition layer was not completely removed and/or where the acetone did not dry thoroughly. Again, only in the Rb series did this procedure not work as well. Nineteen hours elapsed before the air inhibition layer was washed with acetone. All the samples were discolored slightly in small regions. It is assumed that the air inhibition layer was not removed from these zones.

There are two possible reasons why the air inhibition layer caused discoloration of the gel coat. Cobalt, from the promoter, is believed to cause the purple-blue color. It may be concentrated in the air inhibition layer or the air inhibition layer provides a path for cobalt to leach out of the laminate.

The third best procedure was removal by scraping. This was an extremely difficult task. The gel coat was extremely uneven which made it hard to remove material in between ridges. Generally, small but very numerous blisters formed.

A severe purple-blue discoloration appeared in streaks in the gel coat. It seemed to follow the pattern of the ridges. Again, the air inhibition layer is assumed responsible for the discoloration.

Second worst was no treatment at all. Both large and small blisters formed over the entire surface. All samples were severely and uniformly discolored.

Finally, sanding the air inhibition layer produced the worst results. The entire surface was covered with small blisters. The layer is very tacky and therefore very difficult to sand. As a result, this material gets concentrated in areas and probably imbedded into the gel coat from the force of sanding. This gives localized zones of concentrated water soluble material that act as initiation sites for osmotic blistering. Severe discoloration occurred in streaks, again, because it was difficult to sand the layer between the ridges of the gel coat.

Washing the air inhibition layer off with styrene did not improve blister resistance. It performed slightly worse than the sample with no treatment.

Of all peel plies tested, plastic sheet gave the second best results. The problem with plastic is that it pulls the gel coat away from the mold. This results in zones where there is no gel coat to areas of extremely thick gel coat. Blisters obviously occur first and worst in the thin areas. The best results were obtained with coarse nylon cloth peel ply, third with coarse polyester cloth, fourth with fine nylon cloth and the worst blistering occurred with no treatment at all.

Except for plastic peel ply, all the cloth peel plies are pervious to air. Any air that reaches the surface will form air inhibition material. It can only be removed by the "peeling" action on removal. Very little, to hardly any, material was found on the removed cloths.

The following conclusions can be drawn from this study:

1. Wax paper, placed over the wet gel coat, prevents air inhibition.
2. Some sort of peel ply is better than no treatment at all.
3. Removing the air inhibition layer with acetone gave mixed results.
4. Scraping the air inhibition layer off helps only slightly.
5. Removal of the air inhibition layer by sanding gives the worst results.

6. The air inhibition layer is partially responsible for the purple-blue discoloration of the gel coat after exposure to hot water.
7. The air inhibition layer causes smaller and more numerous blisters.
8. If the air inhibition layer is not removed with care, a significant amount of good gel coat can be removed. Any reduction in the gel coat thickness will lead to faster blister initiation.
9. Reduction of air inhibition will not prevent deeper blisters.
10. Air inhibition can be eliminated by continuous lay-up.

4. Water Solubles Associated with Glass Reinforcement

A series of samples were made using an ISO-NPG white gel coat material and an ISO laminating resin with a silica thixotrope. The gel coat thickness was 24 mils. No glass reinforcement was added to the sample. Two layers of resin were added 18 hrs. apart. Each layer was sixty mils thick. The samples were immersed in 65°C water for one year. At the end of that period, the sample had bowed with the gel coat convex, but no blisters were found. When the same gel coat and laminating resin was used to make laminates with veil mat and woven roving, blisters were observed in every case in less than one month.

Microscopic examination of cross-sections showed no blistering. An X-layer was located between the two laminate layers. The cause of this layer is discussed in detail in Section 3. A series of small disk cracks formed in the plasticized zone of the X-layer but did not spread into the birefringent zone of the X-layer. No disk cracks were located in other areas of the resin.

The absence of blisters must be attributed to the absence of glass since the same resin and gel coat had been used in making glass reinforced composites which did blister. Some glass binders must introduce water solubles which begin the disk cracking and osmosis which leads to blistering. These materials are subject to totally different stress conditions than a sample with glass. This could play a role in blister initiation. Furthermore, the lack of glass, which is an effective heat sink, may have allowed the exothermic heating of the resin

in the glass free samples to reach a higher cure temperature than a glass containing composite. Further experimentation must be conducted on this important finding.

One additional observation regarding the disk cracks at the X-layer is important. In the resin, around the disk cracks, there was a depletion of silica filler. The concentration change seems to be related to convective flow in the resin layer. The observation proves that silica thixotrope has a strengthening effect on the polyester resin.

It should be emphasized at this point that other glass free composites have exhibited blisters because of something present in the resin itself. We have reported blistering when sorbitol is added to the resin. Pritchard has reported on the role of excess glycol in the resin in promoting blisters. Of the commercially available resins, the isophthalic resins, without additives or a water soluble glass coating, are more resistant to blistering than orthophthalics and are more resistant than the vinyl ester tested.

Glass can cause blistering either because the glass fibers are water soluble or a coating added to the glass is water soluble. Almost all glass used in the United States is E-glass or some other corrosion resistant glass. The experiments conducted on glass fibers suggest the glass itself is not a problem. This suggests that the coatings on glass can be a cause of blistering.

There are four reasons why a coating is applied to glass fibers. A sizing is sprayed onto glass fibers as they are formed to protect the surface. Added to this size or applied later, a lubricant may be added to protect fibers as they are woven into fabrics or mats. The addition of a coupling agent to form a bond between the glass fibers and the polyester laminating resin is critical to the strength and performance of a composite. Finally, to stabilize a mat or woven structure, a binder must be applied. If any of these components or their carriers are water soluble and are allowed to remain on the fiber during lamination, they will contribute to or cause blistering.

The same resins--ORTHO, ISO, or vinyl can yield a blister-free composite when used with one glass fiber formulation and give a severely blistered composite when used with another glass. Rockett, Rose Florio, Choifere and Trottier, "The Causes of Blistering in Boat Building Materials", Final Report submitted to U.S. Coast Guard. Conversely, as discussed above, those same resins without glass can show blistering if other water soluble components are present.

One set of samples was constructed to study the effects of glass binder and coupling agent on blistering. The "clean" glass (no binder or coupling agent) was donated by a company. A set of samples was constructed using clear ISO/NPG gel coat and ISO laminating resin. Four plies of this glass were used. The samples were immersed in a 65 C distilled water bath.

Following approximately one year of immersion, no blisters were evident on the sample. Only a few tiny blisters had formed as a result of the glass debonding from the resin directly beneath the gel coat. These samples were cross-sectioned and examined under a light microscope. A photomicrograph of a cross-section is shown in figure 1. The greenish discoloration in the glass fibers appears to be a light absorption effect. No disk cracks were found in the sample. The only sign of water damage was severe debonding of the glass from resin.

The reason sample did not disk crack or blister may be attributed to the absence of binder or coupling agent. No corrosion of the glass fibers was evident. Previous work, conducted on several panels, constructed with chopper gun roving, showed severe blistering. This suggests that chopper gun roving have been a sources of water soluble material. Microscopic observations indicated that there is a substantial amount of binder holding the fibers together. Burnout tests on various glass fibers show they can contain as much as 6.5 % binder. It is believed that the binder may be PVA (polyvinyl acetate) which is water soluble.

To determine the material that could be leached from a glass surface, weighed strands of glass roving were placed in purified water at 65°C for 18 months. The pH of the solution was followed and it dropped from 7 to 6.6. If the leached

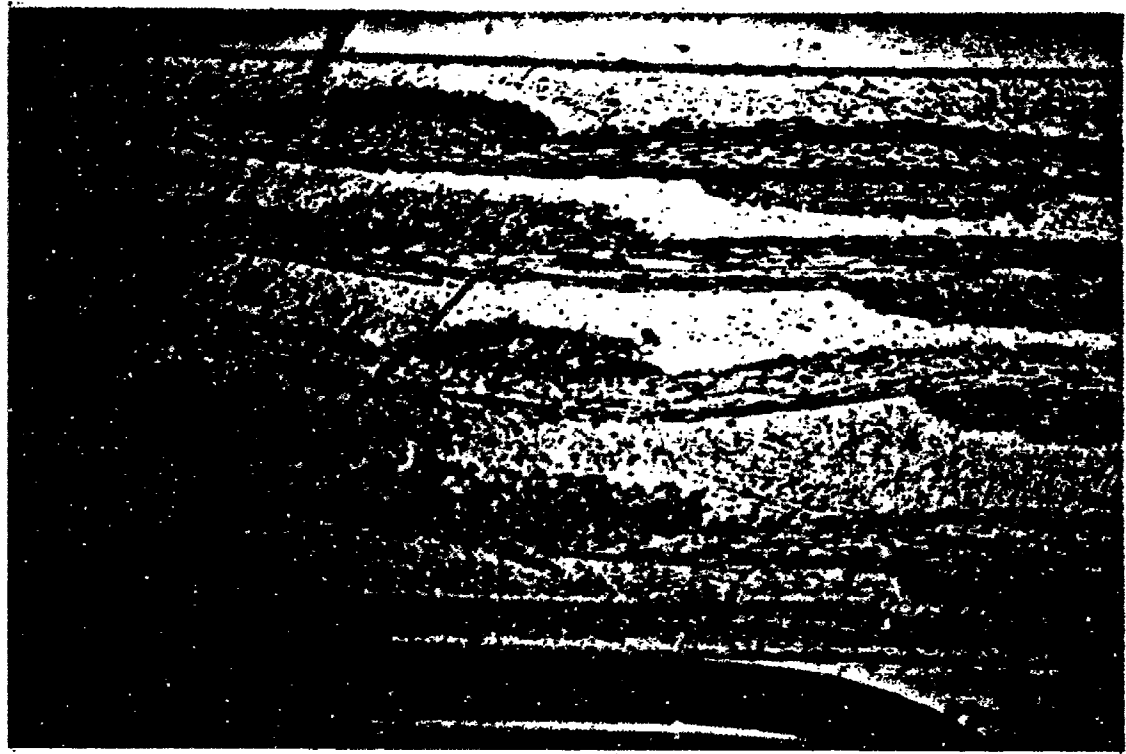


Figure 1. Photomicrograph of Composite with ISO/NPG Gel Coat and Iso Laminating Resin and Reinforced with "clean" Glass, Following Exposure to 65 C Water for One Year.

material had been polyvinyl acetate (PVA), a commonly used emulsion binder for glass, the pH should approach 3. The fact that it stayed so high suggests that either no PVA was used or as it leached off the glass, some basic component from the glass also went into the water, thus off-setting the acid effect. The solution has a strong glycol odor. To determine the exact nature of the solution mass spectroscopy gas chromatography and atomic absorption tests were conducted. Mass spectroscopy-gas chromatography results showed six peaks. Water gave the strongest peak. The organics found, listed in decreasing order of amount, were phenol, acetone, acetophenone and in trace amounts, cumene and 2-phenol - 2-propanol.

These constituents must be coming from the glass binder, the coupling agent or the rubber stopper that sealed the flask containing the immersed fibers. These materials could not have come from the decomposition of PVA in water. Phenyl groups, because of their size, are extremely unlikely to be found in glass coupling agent compounds. The strong glycol odor can be attributed to phenol.

Atomic absorption gave the following results:

Ca²⁺ - 135 ppm
K⁺ - 394 ppm
Na⁺ - 76 ppm
Al³⁺ - less than 1ppm
Si⁴⁺ - 33.6 ppm

Ion leaching is common for some types of fiberglass. Leaching is caused by hydrogen ions, in the water, exchanging with metal ions in the interstitial sites of the glass network. Sodium ion leaching is most common. This leads to the corrosion or break down of the glass network. This will appear as a gel like phase on the glass surface. The layer is anywhere from 10-100 angstroms thick and would be below the range of visible microscopy. Examinations of these fibers after 6 and 18 months, at 600X and 1000x, showed no evidence of such a layer.

The atomic absorption results show that the leachants are in relatively low concentrations. Little breakdown of the glass network took place. Because the sodium ion concentration is so low, this must be an extremely low sodium glass.

The most predominant leachants are calcium and potassium ions. If the glass is assumed to contain a reasonable amount of calcium oxide (10 per cent), then for the weight of glass fibers and water used, if all the calcium leached out, the solution would contain approximately 2400 ppm of calcium ions. The calcium ion concentration found, of 135 ppm, is 5.6 % of the estimated total present. This is a substantial amount. Some corrosion of the glass fibers should have been seen.

Breakdown of polyester is known to happen both in an acidic and a basic environment. Basic attack is more severe than acid attack. One possible sequence of events leading to glass-associated blisters would involve absorption of water at the glass-resin interface, followed by the formation of micro-cracks, due to swelling from water absorption. The water leaches metal ions hence forming a basic solution. This basic solution breaks down the adjacent polyester causing a solution concentration change. In addition, some of the organics found are water soluble and would be found concentrated around the glass fibers. Both these factors could cause osmotic pressure to build and blisters to result.

Additional work must be done on the role of glass and other reinforcement fibers in the blistering of polyester composites.

5. Swelling Stresses produced by Diffusion

Implanted strain gauges were used to determine swelling stresses produced by water diffusion.

Strain gauges were implanted in three different composites. The first was constructed with both an orthophthalic acid based laminating resin and gel coat (ORTHO/ORTHO). The second was constructed with both an isophthalic acid based gel coat and laminating resin (ISO/ISO). The third was constructed with an isophthalic acid based gel coat and orthophthalic acid based laminating resin (ISO/ORTHO).

Gauges were implanted at four different depths into the laminate; Gauge #1 - in the gel coat, gauge #2 - between the gel coat and veil mat, gauge #3 - between the veil mat and first layer of roving, gauge #4 - between the first two layers of roving.

All samples were placed in a 65°C water bath for single sided exposure. Stress data was taken daily and samples were checked periodically for blister initiation and severity. Results obtained are given in figures 2 and 3 and show stress vs time vs depth data.

From the results it can be seen that the stress level remains fairly constant initially. After a period of time, depending on the depth of the strain gauge, stress or tension appears to increase until the reading goes off scale or begins to fluctuate erratically.

The smoothly varying portion of the data reflects the fact that as water is being absorbed into the polymer it swells. Strain gauges measure electrical resistance, which is proportional to the amount of stretching or compressing of the gauge. By implanting gauges at various depths into the laminate, the depth of penetration of the diffusing water front can be determined by assessing the time at which an abrupt rise in stress begins. As the water front approaches the gauge, the gauge goes into tension. The data clearly shows that gauge #1 expands first and the other gauges, farther back, follow a similar trend with a time delay. Gauge #4, farthest back, sees little or no effect from water for the time of experimentation.

After a certain point the data will usually begin to fluctuate erratically. At this point it is believed that the data is no longer reflective of the true stresses inside the laminate. It is believed that these fluctuations can be attributed to water molecules condensing onto the strain gauge or the gauge debonding from the polyester matrix. Also, after prolonged exposure to water, the polymer film, that encapsulates the strain gauge, begins to peel apart. Occasionally the polymer will be subject to greater than a five percent strain. Once the gauge sees a five percent strain it becomes useless since this is the

Figure 2.—stresses due to water immersion
ortho/ortho laminate (55°C)

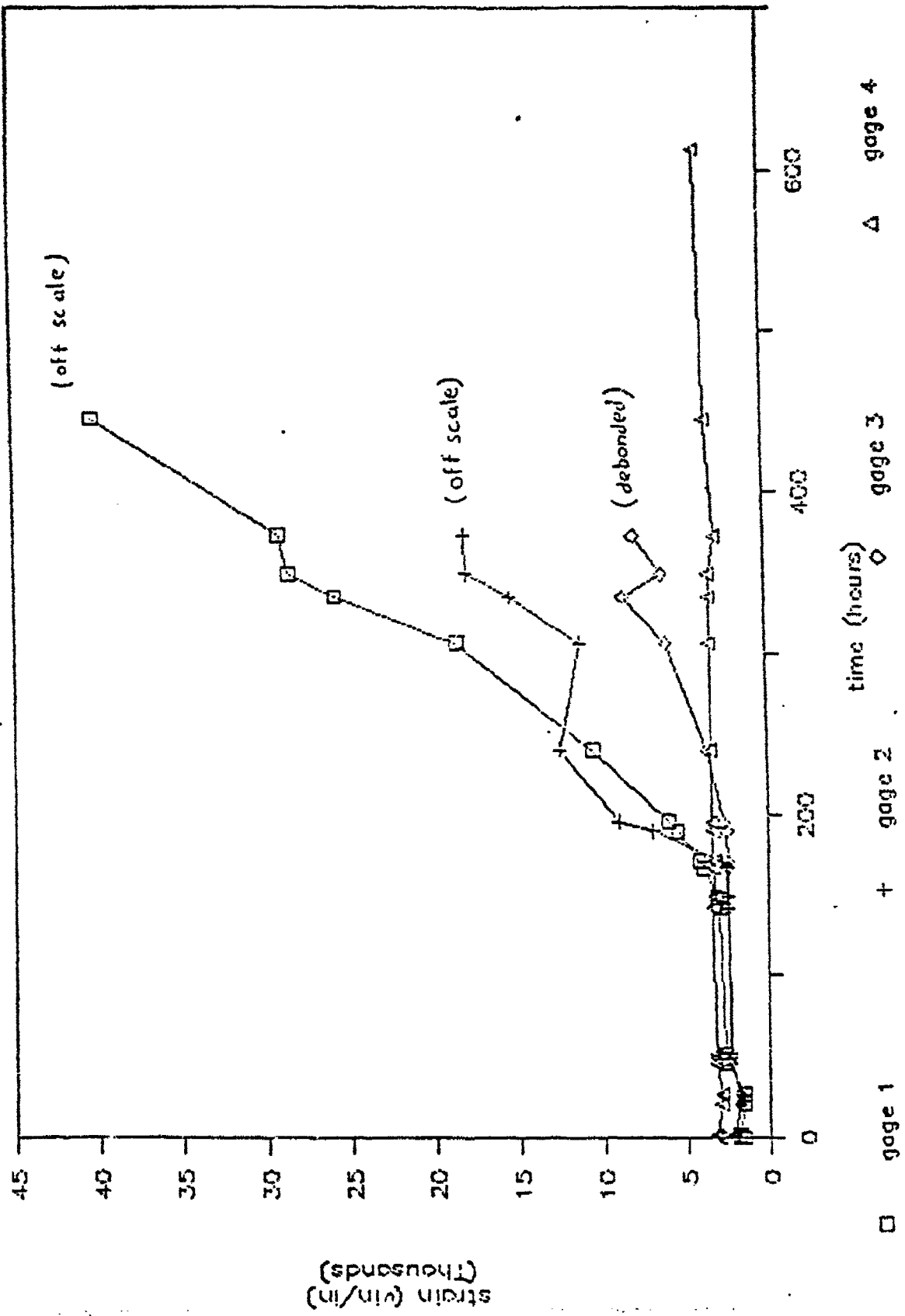
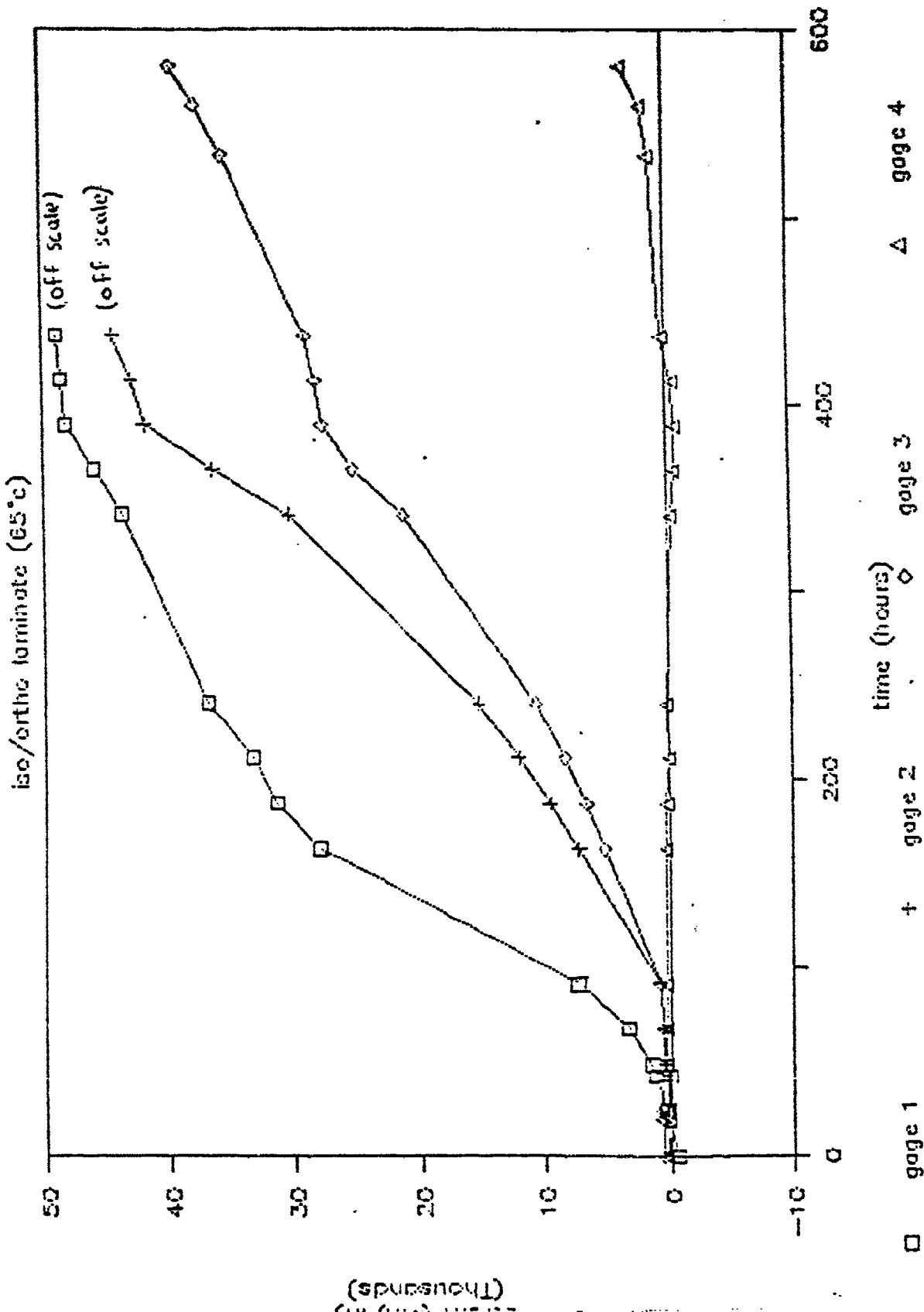


Figure 3. —stresses due to water immersion



limit of the strain gauges used.

For these reasons it is felt that the strain gauges are most useful in assessing the stresses produced as a result of the diffusing water front. Once the polymer nears saturation readings become unreliable.

No direct relationship was established between the onset of blistering and stress levels. Some of the data seems to suggest that blisters are initiated once the stress level difference between the gel coat and the veil zone becomes appreciable. Further work is still needed in this area.

No conclusions were drawn on the differences in the stress levels produced among the different composites tested. Preliminary results seem to indicate that increased stress levels occur sooner in the ISO/ORTHO composite than in the samples made of like gel coat and laminating resin.

The data does reinforce our belief that stress plays a key role in blister initiation. Figure three shows that on swelling, the gel coat has expanded by 40,000 micro inches per inch or four percent. That means that if a gel coat was free to expand, below the water line, the gel coat on a 25 foot boat would elongate by 12 inches. Constraining forces prevent free expansions. Stresses, therefore, build-up, especially near the water line.

These stresses proceed the water front. When the area saturates with water, the clusters of water molecules align in disk shaped units perpendicular to the maximum stress direction. These water clusters condense to form disk cracks which contain water. Extraction of water soluble molecules from the surrounding resin produce acidic solutions more concentrated than the outside water. This begins osmosis which produces blisters.

6. Long Term Damage by Water Absorption

In spite of the improved understanding of blistering developed in recent years a basic question remained. Is blistering and water absorption only a cosmetic and surficial problem or does deep seated damage occur after prolonged water exposure? The following experiments were conducted to obtain information on this important question.

Samples, which were immersed in water at 65°C for over a year were cross-sectioned and examined under the light microscope and with the scanning electron microscope to determine the types of internal damage which could lead to strength deterioration which is reported in the following section. Four types of long term damage were observed. These include "deep blisters", polymer degradation, extensive disk cracking and debonding of glass from resin. Almost every sample

showed the type of blisters which form just below the gel coat in the veil mat region. As osmotic pressure develops in this region the gel coat begins to deform. This produces the surface bumps known as blisters. In 65 C water, these form on orthophthalic or isophthalic type composites after 100 to 1000 hours. The amount of time is governed by factors such as the thickness of the gel coat, the presence of an air inhibition layer on the inner gel coat surface, the type of glass binder used, etc. After a year of immersion, these near surface blisters are larger and more abundant. Some of the blisters crack open to form a craze pattern on the gel coat surface. Single long blisters sometimes develop along continuous glass strands.

In the composites exposed for long periods, deeper "blisters" are encountered below the veil layer and inside the woven roving zones to a depth of 1/4 inch and more. Such deep seated "blisters" are shown in figures four and five. The first figure is a scanning electron microscope image. Second is a thin-section light micrograph. This deep-seated damage, although caused by identical mechanisms as those operative in near surface damage, do not appear as blisters on the gel coat surface because the composite, at this depth, is reinforced with glass and cannot bulge outward. Rather, the osmotic pressure forces the composite to separate and an internal crack will spread parallel to the gel coat surface. The term, "deep osmotic cracks" will be used to refer to this type of damage. The ultimate result of this type of damage will be delamination of the hull. Deep osmotic cracks are found, after a year at 65°C, in composites made with both orthophthalic and isophthalic laminating resins.

In all cases, the deep osmotic cracks are located near or in fiberglass strands in the woven roving. The location of the cracks, at these positions, may be due to one of the following four reasons:

1. A higher concentration of water soluble material is associated with the glass binder. The difficulty with accepting this explanation is that the binder concentration should be the same on all parts of the glass strands. Note that in figure four an osmotic crack did not form near the top most strand in the composite which is subjected to water longer than the strand where cracking did take place.



Figure 4. Scanning Electron Micrograph of Deep Osmotic Crack Within Woven Roving Zone of the Composite. Near surface gel coat blister is also shown in the veil mat. Note the disk cracks around the osmotic crack.



Figure 5. Transmission Light Micrograph of an FRP Thin Section. This section also shows veil mat blisters and deep osmotic cracking in the woven roving zone.

2. The resin is weaker or more brittle in the region where cracking occurs. Slight inhomogeneities in catalyst concentration caused by poor mixing could explain the position.
3. Within each layer there are inhomogeneities caused by the non-wetting of the fiberglass strand by the lay-up resin. Figure four shows clearly that such zones exist. Only in one case did an osmotic crack appear to be associated with such a void.
4. Finally, and most probably, the crack location is controlled by swelling stresses caused by the severe mismatch in elastic moduli between the unreinforced zones of the composite and the zone that is reinforced with glass strands.

The second type of long term damage which was observed after one year or more, is the degradation of the polymer near blisters. On blister walls, there is evidence that the acidic blister fluid is degrading the polymer. A thin zone of chalky or punky material is formed around the blister. This zone appears to be only a few microns thick.

A third type of long-term damage observed is extensive disk cracking throughout the laminate. Examples of extensive disk cracking are shown in figures six and seven. Figure six shows a micrograph of an isophthalic gel coat and resin sample produced by a local boat manufacturer tested in our laboratory. The sample was exposed to water at 65°C for one year and 25°C for another year. Figure seven shows a micrograph of a sample with a type of vinyl ester based gel coat and orthophthalic laminating resin. This sample, as well, was produced by a boat manufacturer and was tested in the laboratory. It was exposed to water at 65°C for about a year. Another observation shows disk cracking below veil mat blisters. Under one of the near surface blisters, a zone of numerous stress produced disk cracks was observed. The zone radiated hemispherically from the bottom of the blister. The cap of the blister had cracked allowing water directly into the blister cavity. This has a major effect on the water uptake of the resin beneath the blister



Figure 6. Photomicrograph Showing Extensive Disk Cracking in an ISO/ISO Laminate, Following Exposure to water at 65 C for One Year and Another Year at 25 C.



Figure 7. Photomicrograph Showing Extensive Disk Cracking in a Composite Constructed with a Type of Vinyl Ester Gel Coat and Ortho Laminating Resin, Following Exposure to Water at 65 C for Approximately 1 Year.

Disk cracks form in a polymer when the polymer becomes saturated with water. At saturation, diffusing water molecules tend to cluster in spheres. If a stress is present, these spheres become disk shaped (1). The clusters join together to initiate disk cracks. These disk cracks, containing water, concentrate low molecular weight species. This solution begins the osmotic process which results in blisters. Disk cracks can also be formed by thermal stresses. Curing stresses will also produce disk cracks. If an inch of resin is placed in a beaker, catalyzed and allowed to cure, disk cracks will be seen to form after an hour. (REF. : S.B. Lee and T.J. Rockett, Personal Communications, 1988). The morphology of those dry disk cracks is identical to the morphology of those disk cracks formed in boat hull materials by water saturation.

6. Disk cracks relieve swelling and curing stresses. Once these stresses are relieved, the crack growth stops unless acted on by a new stress. Osmotic pressure is one such stress which opens disk cracks and causes blistering. Osmotic pressure is the pressure difference caused by chemical concentration differences between two solutions which are separated by semi-permeable membranes. The gel coat and laminate, between the disk crack and the solution (sea water) outside the gel coat, act as a semi-permeable membrane. Water can diffuse into the F.R.P., but the larger water soluble constituents, in the disk crack solution, cannot diffuse out. Chemical equilibrium demands that the chemical potential (μ) of water in the disk crack becomes equal to that in the external solution (sea water) so that the following relationship is fulfilled:

$$\mu_{\text{H}_2\text{O}} (\text{disk crack}) = \mu_{\text{H}_2\text{O}} (\text{sea water}) \quad (6.1)$$

To a first approximation, equation 6.1 is satisfied when the internal concentration of water within the disk crack equals that of the sea water, which is approximately 3.2 weight percent salts or 96.8 weight percent water. If the inner solution contains this much water or more, no osmotic pressure is developed and no crack growth is observed. The disk crack solution takes up water soluble constituents, if they are present in the polymer, and concentrates them, reducing the percent of water in the disk crack. Now there exists a chemical driving force to draw water into the disk crack. Water will continue

to enter the disk crack until the inner osmotic pressure, π , equals the confining pressure around the growing blister or until the internal water soluble constituents are diluted to 3.2 weight percent. The force of the osmotic pressure is given by the relationship:

$$\pi = \frac{\mu_{H_2O}(\text{disk crack}) - \mu_{H_2O}(\text{sea water})}{V} = \frac{RTX}{V} \quad (6.2)$$

where V is the volume of the solution, T - temperature, R - the gas constant and X - the total number of moles of all water solubles in the disk crack solution. Osmotic pressures, calculated from equation (6.2), for blister solutions of concentrations similar to those found in blisters, are approximately 1,500 psi. Propylene glycol was assumed to be the sole water soluble constituent for these calculation. This value is close to the values calculated earlier. This pressure is too low to fracture a polyester. The tensile strength range of polyesters is 6,000 to 20,000 psi. The osmotic pressure developed, however, is not too low to propagate a crack once it is opened.

A stress applied to a material is magnified at the tip of any crack present in the material. Inglis found the relationship to be

$$\sigma_{\max} = \sigma_a \left(1 + 2\sqrt{\frac{a}{\rho}} \right), \quad (6.3)$$

where σ_{\max} is the stress at the crack tip, σ_a - the stress applied normal to the disk crack, a - half the major axis of the crack and ρ - the radius of the crack tip. The term under the square root is defined as the stress concentration factor, K . Examination of disk cracks show that K can easily reach 20. Therefore, if the applied osmotic stress is 1500 psi, then the stress at the disk crack will be 31,500 pounds per square inch which will cause the disk cracks to grow.

The second type of stress which may cause disk cracks to grow are those stresses produced during boat use. If the hull polymer has a strength of 10,000 psi and sailing stresses of 500 psi, this would be sufficient to cause disk crack

growth. Convergence of cracks can produce internal delamination.

Most disk cracks are found just beneath the gel coat. This is also the location of most initial blisters. However, after prolonged periods of time, as the water ingresses deeper into the laminate, disk cracks are formed deeper within. Also, water diffusion from the back side of the laminate must be considered. This does not affect blister initiation time for those found just beneath the gel coat, but it may affect the onset times of deep osmotic blisters. An example of a sample containing deep osmotic blisters is shown in Figure 8. Some samples show extensive disk cracking on the back side of the laminate.

Diffusion of water through the backside of the laminate is a realistic factor for both the experimental set-ups used in this study and for boats. In the experimental set-up either both sides of the sample see water or only the front side (single-sided exposure). On one sided exposure experiments, the backside of the samples, in the tanks, see 100 percent relative humidity or close to it. The rate of diffusion of water into a polymer is identical in liquid water and in 100 percent relative humidity. For boats this is a realistic factor as well. The bilge of a boat, during use, always contains some water and the humidity is probably close to 100 percent.

The fourth type of long-term damage observed is the debonding of glass fibers from the resin. Figures nine and ten show evidence that disk cracks, near glass fibers, lead to the debonding of glass fibers from polyester resin. This is most evident in the heavily reinforced zones of the composite.

If the disk crack is near a bundle of glass fibers, it will grow towards the fibers. Once a load is applied to a resin/glass fiber composite, the load is transferred from the glass to the resin or vice-versa. The stress is amplified by a factor inversely proportional to the radius of the glass fiber. Particularly in closely spaced glass fibers, this forms a highly stressed zone at the polymer/glass interface. The stress at the interface is further amplified because of the severe mismatch of elastic moduli between the glass and the resin. To further complicate matters, the region of polyester resin between the glass



Figure 8. Photomicrograph of "Deep Seated" Blisters Found in an ORTHO, ORTHO Composite after 4106 Hours of Exposure to 65 C Water.

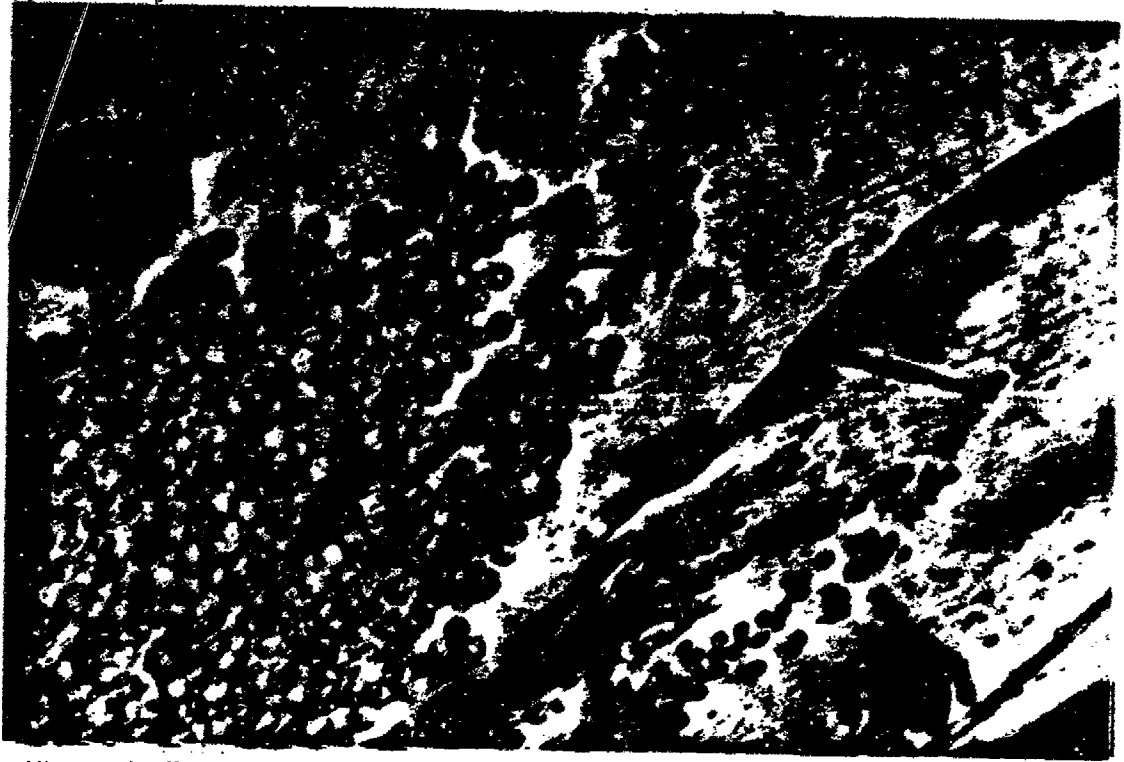


Figure 9. Photomicrograph of Disk Cracks Near Glass Fibers Leading to Debonding.



Figure 10. Photomicrograph of Disk Cracks Near Glass Fibers Leading to Debonding.

fibers is already stressed. Shrinkage on cure produces tensile stresses in the resin, at the interface, because the glass fiber is restraining the resin from shrinking during cure.

The disk crack will grow in the direction which is weakest and/or most highly stressed, which in this case would be towards the glass/resin interface. Since the glass/resin interface is the weakest zone in the composite it will fail first. This leads to debonding. The crack will propagate through the glass bundle by debonding more glass fibers. This sort of failure leads to strength loss of the composite and to the formation of deep osmotic cracks.

Figure 11 shows deep osmotic cracks extending from one glass bundle to another. Such a crack begins in one glass bundle and spreads because of osmotic pressure through the resin, to the adjacent glass bundle.

It must be kept in mind that the damage observed is accelerated by the 65°C (150°F) temperature. If only the rate is affected by the temperature increase, the same damage would be produced in 60°F water after a continuous immersion of 32 years. However, there are, in addition to temperature change, three things that are different in boat use. Two of these factors make our test less severe and one makes our test more severe. The normal flex stresses produced by boat use exacerbate the damage. There are no fatigue stresses in our tests. The second factor that makes our test less severe than boating conditions is that once our test samples are placed in the water bath the samples are post-cured at 150°F. Normal boating materials are usually not subjected to any elevated temperature post cure. Literature references show post-curing improves resin properties. The factor that makes the 65°C (150°F) tests more severe than boating conditions is the saturation value of water in the resin. While resins at 60°F can take in less than 1 percent water at saturation (approximately 0.8 weight percent), they can take up about 1.3 percent water at 150°F. This means that the swelling stresses produced will be about 30 percent more severe. Exactly how these factors balance out is not known. It is almost certain that the 32 year figure to produce similar damage is too high.



Figure 11. Photomicrograph of "Deep Osmotic Cracks" Bridging Between Two Bundles of Glass Fibers.

At any rate, the data clearly show that with continuous immersion and saturation of hull material, these polyester resin composites have a finite life. The only prevention to long term damage is to keep the water out of the composite by using thicker gel coats, adding a barrier coat and replacing these barrier coatings every year or two, and keeping the bilge side as dry as possible to prevent inner saturation.

The strengths of various glass reinforced composites were evaluated after prolonged exposure to water. When a sample was made for blister evaluation, a section was removed and held at room temperature while the remainder was exposed to water. Test samples, cut to the following dimensions: 4" X 0.4" X 0.2" and a 1.0" gauge length, were milled so that the center section of the specimens had a cross-sectional area of .02-.04 square inches. Such standard tensile samples were made for both the dry and wet composites. Table 2 shows the strength data obtained by breaking the samples with an Instron stress-strain unit.

The first set of samples, made with orthophthalic acid based laminating resin, (#41) show a 50.1 percent reduction in strength after single sided exposure to water at 65°C for 0.3 years and an additional year of total immersion exposure at 27°C. Data from Norwood and Marchant suggest a decrease in one year strength, at 30°C, of about 25 percent for orthophthalic resins (2). Their data suggests a 20 percent decrease after a year for isophthalic resin.

Our second set of data on orthophthalic gel-coated composites with orthophthalic resins show a 44 percent reduction in tensile strength even though the exposure conditions were more severe. The tests on the isophthalic resin with isophthalic gel coat composite showed the following surprising results: although the starting strengths were higher in the case of the isophthalic material than the ortho, the reduction in strength after a year was 83 percent. A second set of tests was made on series 95 which also had an isophthalic laminating resin. This series showed a 73 percent reduction in strength after 1.1 years. There are many literature references that point to improved water resistance of isophthalic acid resin vis-a-vis orthophthalic acid resins. These contradictory results could be caused by the fact that we did not post-cure the samples at elevated temperatures before testing. However, the samples are "post-

Table 2

Strength Data for F.R.P. Sample Before and After Exposure to Water.

Sample Number	Type	Age (yr)	Exposure Conditions	Test	Strength (psi)
41-N-1	ortho/ortho p.g.	1.3	Ambient	tensile	31,370
41-N-2	ortho/ortho p.g.	1.3	Ambient	tensile	29,310
41-N-3	ortho/ortho p.g.	1.3	Ambient	tensile	25,630
41-B-1	ortho/ortho p.g.	1.3	.3 yrs. @65°C ¹ /1 yr. @25°C ²	tensile	15,700
41-B-2	ortho/ortho p.g.	1.3	.3 yrs. @65°C ¹ /1 yr. @25°C ²	tensile	14,320
41-B-3	ortho/ortho p.g.	1.3	.3 yrs. @65°C ¹ /1 yr. @25°C ²	tensile	13,220
(percent reduction in strength = 50.1%)					
65-H-1	ortho/ortho p.g.	1.3	Ambient	tensile	37,360
65-H-2	ortho/ortho p.g.	1.3	Ambient	tensile	47,320
65-H-3	ortho/ortho p.g.	1.3	Ambient	tensile	44,090
65-F-1	ortho/ortho p.g.	1.3	.33 yrs. @65°C ¹ /1 yr. @65°C ²	tensile	24,190
65-F-2	ortho/ortho p.g.	1.3	.33 yrs. @65°C ¹ /1 yr. @65°C ²	tensile	20,420
65-F-3	ortho/ortho p.g.	1.3	.33 yrs. @65°C ¹ /1 yr. @65°C ²	tensile	27,370
(percent reduction in strength = 44%)					
93-A-1	iso/iso	1	1 yr. @65°C ²	tensile	4,440
93-A-2	iso/iso	1	1 yr. @65°C ²	tensile	7,640
93-A-3	iso/iso	1	1 yr. @65°C ²	tensile	11,600
93-A-4	iso/iso	1	1 yr. @65°C ²	tensile	6,790
93-D-1	iso/iso	1	Ambient	tensile	---
93-D-2	iso/iso	1	Ambient	tensile	56,500
93-D-4	iso/iso	1	Ambient	tensile	32,500
93-D-5	iso/iso	1	Ambient	tensile	49,900
(percent reduction in strength = 63%)					
95-G-1	ortho/iso	1	1.1 yr. @65°C ²		11,400
95-G-2	ortho/iso	1	1.1 yr. @65°C ²		17,500
95-G-3	ortho/iso	1	1.1 yr. @65°C ²		17,400
95-D-1	ortho/iso	1	Ambient		54,400
95-D-2	ortho/iso	1	Ambient	(sample damage)	
95-D-3	ortho/iso	1	Ambient		62,500
(percent reduction in strength = 73%)					

- 1 - Indicates single sided immersion
2 - Indicates double sided immersion

cured" in the water bath at 65°C during testing. More data is required to explain the discrepancies between this data and previous reports.

Figure 12 shows four typical stress-strain curves of composites before and after prolonged exposure to hot water. Each of these are for a sample with a cross-sectional area of 0.022 square inches. While the reduction in ultimate tensile strength is much higher for iso than has been reported previously, the toughness deterioration is even greater. The values given in this report are close approximations. To get exact values, true stress-strain curves must be obtained. The data presented here is engineering stress-strain. Nevertheless, the area under the stress-strain curve is a measure of the toughness of the sample. Toughness of a material is extremely important because it determines how resistant the material is to failure by crack propagation under peak loads. Two materials can have the same ultimate tensile strength (U.T.S.) and radically different toughnesses. Toughness is more important to design and boat life than is ultimate tensile strength provided the latter value is above an acceptable limit. The toughness of the orthophthalic material dropped 78 percent but the isophthalic material dropped in one case 96 percent and in the other case 93 percent. This value for isophthalic resin is also unexpected in light of the fact that they are more resistant to water breakdown than are orthophthalics.

While strength and toughness changes considerably during water exposure, the moduli of elasticity for both isophthalic and orthophthalic materials did not drop appreciably. Values for iso resins averaged 5.2×10^5 (dry) and 5.5×10^5 (wet). Values for ortho resins are 5.2×10^5 (wet) and 4.9×10^5 (dry). These values are in pounds per square inch.

One additional observation worth noting regards the type of fracture observed. While most fractures showed some tearing out of fibers from the resin matrix, the 98 series of iso resins showed a very sharp break after water immersion. The propagating crack goes directly through the glass fiber with little pull out. The inability of the material to deflect the crack accounts for the low toughness of the material. The glass must have lost strength during water exposure or the glass polymer interfacial strength increased and prevented fiber pull-out.

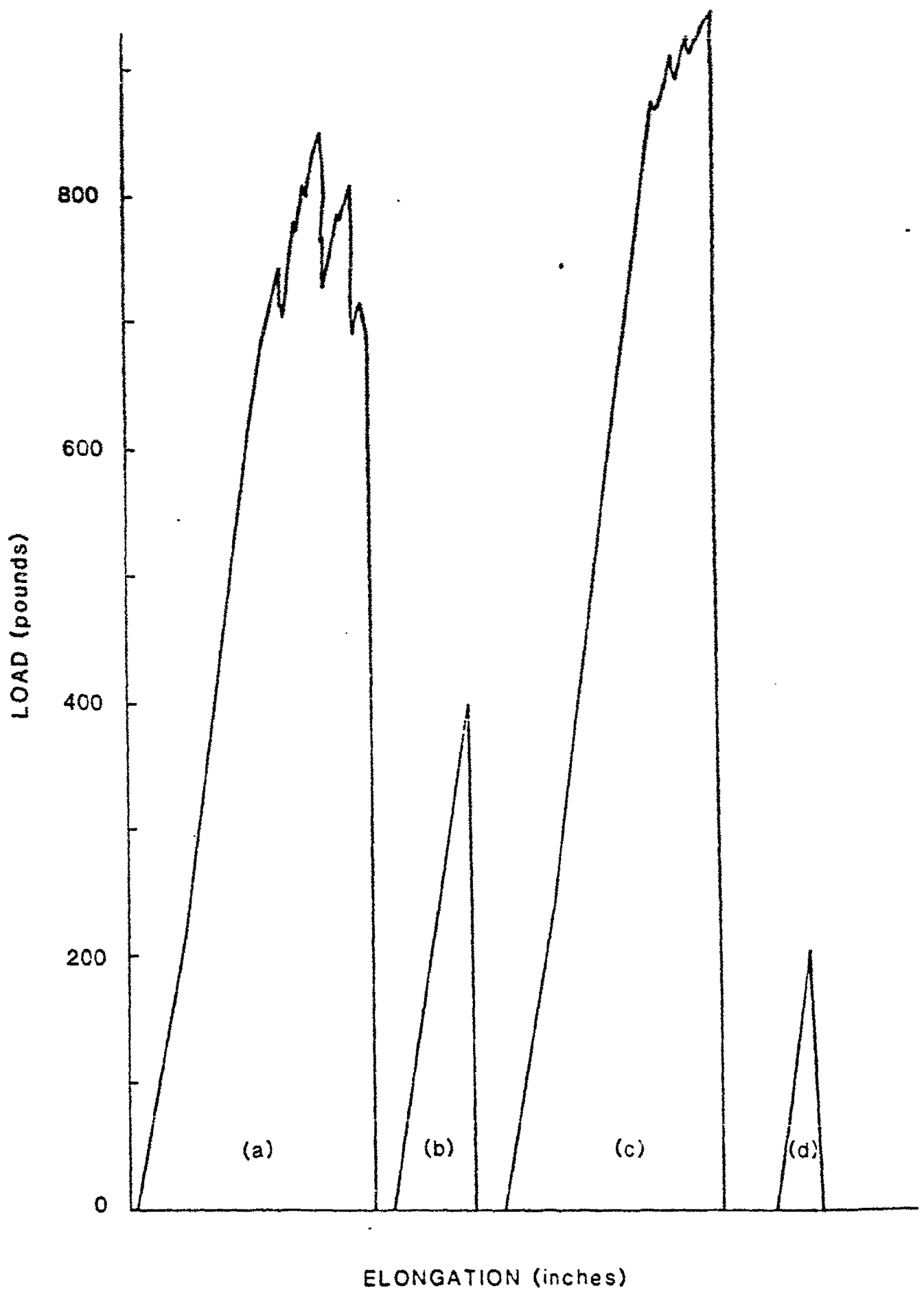


Figure 12 Stress-strain curves for various composites. a-ortho.dry. b-ortho.wet. c-iso.dry. d-iso.wet

While the unanswered questions regarding toughness deterioration demand additional experimentation, it is clear that if boats become saturated throughout their thickness, deep-seated damage will occur limiting the life of the hull.

7. Effect of the Gel Coat on Leaching of Water Soluble Material from Laminates

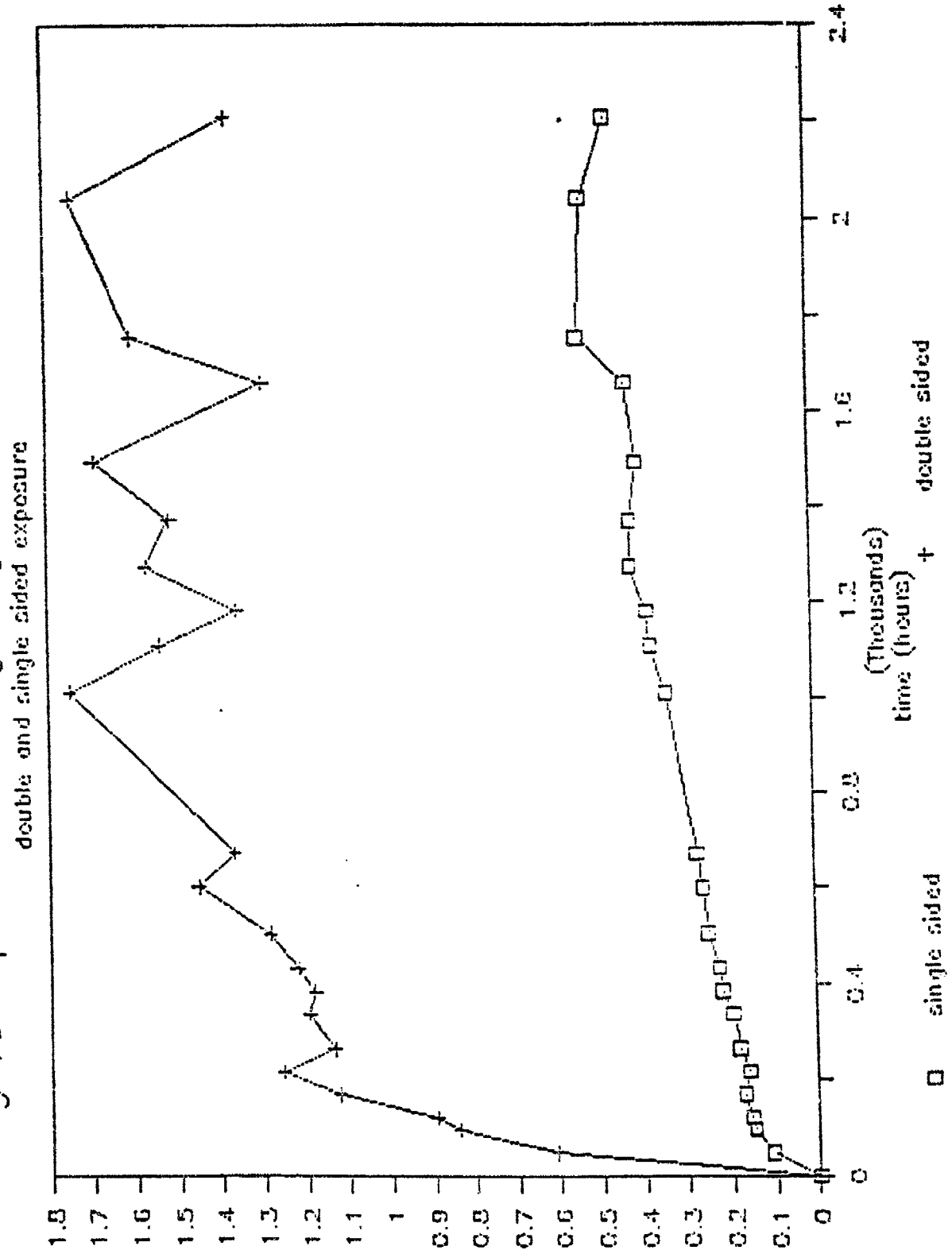
Experiments were conducted to obtain an understanding of the effect of the gel coat on the leaching of water soluble materials from laminates. Two sets of samples were tested. Both have an orthophthalic acid based back-up resin reinforced with woven roving. One has an orthophthalic acid based gel coat (ortho/ortho) and the other set has an isophthalic acid based gel coat (iso/ortho). All samples were immersed in water at 65°C. Two samples of each set were totally immersed and two were subject to single sided immersion. Samples were weighed and checked for blister initiation periodically. Data is presented in figures 13 and 14.

There was no substantial difference in blister initiation time, for identical samples, between the single sided and totally immersed samples. These results are consistent with preliminary observations made in a previous study. This is an important finding since it reaffirms the value of blister initiation data taken on totally immersed samples. Indeed, there was little difference in blister initiation time between the two sets of samples. The first of the four iso/ortho samples blistered in four days and the others blistered in eleven days. The ortho/ortho samples blistered in three to nine days.

The totally immersed iso/ortho samples show a continuous weight loss after 100 hours of immersion. All of the weight gain is due to water pick up. The weight losses are due to three mechanisms: outgassing of small molecules, especially unpolymerized styrene (Ref: Lee & Rockett), leaching of small molecules and solubility of exposed polymer.

After approximately 2300 hours, the rate of weight loss increases abruptly. This is due to the rupturing of some blisters. However, in the case of the

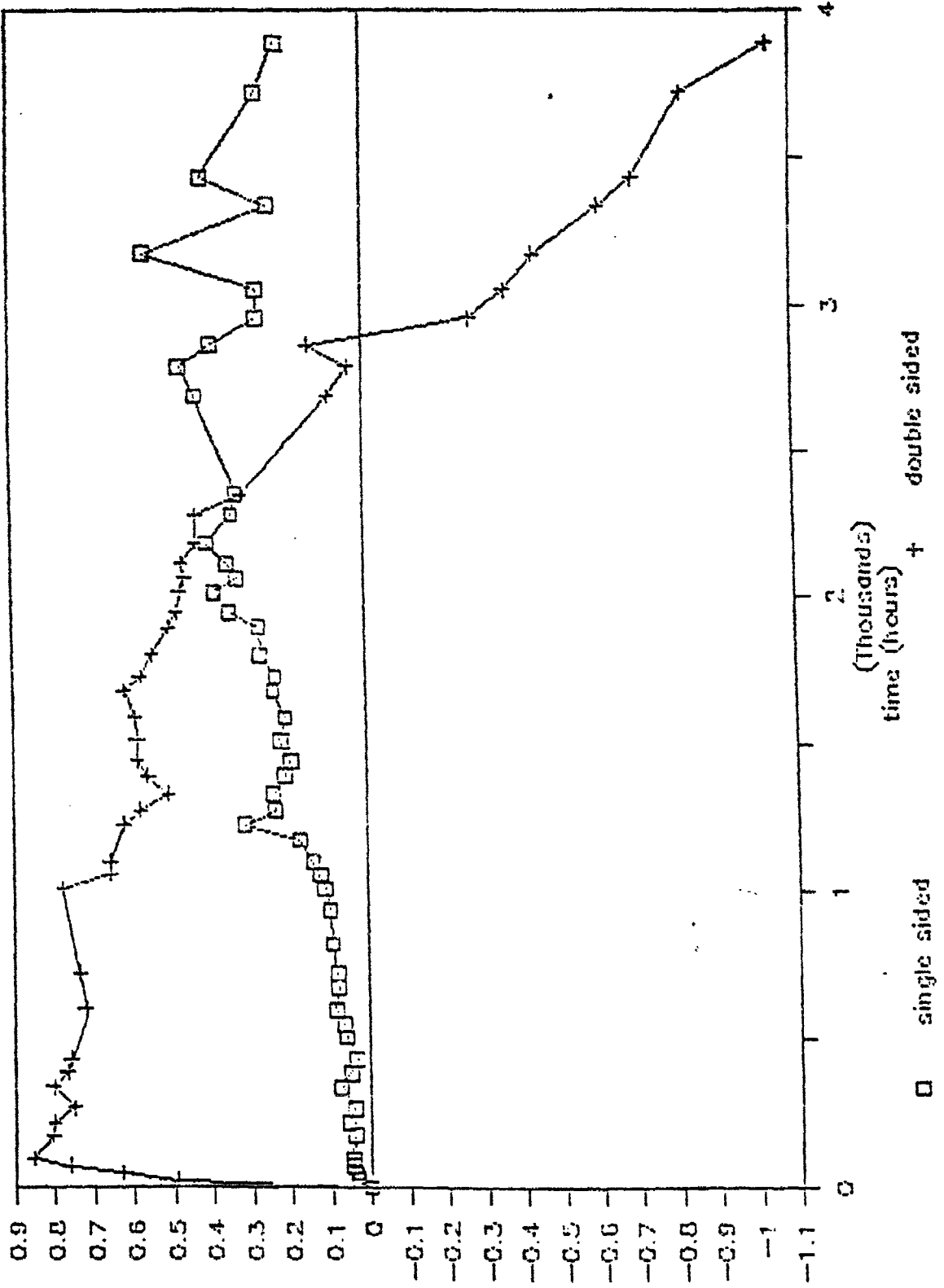
fig 13 - percent weight gain (ortho/ortho)



% weight gain

fig. 14 - percent weight gain (iso/ortho)

double and single sided exposure



ortho/ortho totally immersed samples, this weight loss was not seen. This is consistent with data obtained in a previous study in which ortho/ortho samples did not start to lose weight until after 2700 hours.

There are two reasons why weight loss is delayed in these samples. First, the amount of exposed polymer, on the back of the more glass rich surface of the ortho/ortho sample, is much less than the resin rich back of the iso/ortho samples. Because of this smaller area of polymer exposed to the water, slower leaching, slower outgassing and less dissolution takes place. All of these mechanisms are still operative but at a slower rate. Further, the ortho/ortho sample picks up more water than the iso/ortho sample. As in all of the samples, the weight gain off-sets the weight loss.

Both single sided and immersed iso/ortho and ortho/ortho samples were still gaining weight at the end of the experiment. This clearly shows that the gel coat material retards the rate of leaching of water soluble materials, and outgassing and is far less susceptible to solubility than the air cured resin. The ortho/ortho samples pick up more water than the iso/ortho samples but at a somewhat slower rate. There are three reasons for this. First, water is more soluble in orthophthalic acid based resins than it is isophthalic acid based resins. Secondly, the resin has a lower tensile strength and therefore more disk cracks can form. Thirdly, ortho is more flexible than iso which means that growing blisters do not crack open as quickly.

Figure 15 shows the back surface of a fully immersed sample and one exposed to water on the gel coat side only. The surface not exposed to water is in excellent shape. The surfaces exposed to water show a severe crazing pattern due to the shrinkage produced by leaching and growth of disk cracks to the surface. It is obvious that gel coats protect the resin from this type of damage. However, and here-in lies the dilemma of the gel coat. The gel coat prevents the loss of small molecules from the resin. These molecules get trapped underneath the gel coat this allows them to create osmosis which causes blistering.

a.)



b.)



Figure 15. Photomicrograph of the Resin Rich Backside of a Composite that Has a.) Not Been Exposed to Water b.) Been Exposed to 65 C Water .

Figure 15 also shows the importance of keeping the bilge as dry as possible. This point has already been emphasized. The physical damage to the resin which weakens it, speeding up saturation of the hull and the increased osmotic cracking is shown dramatically in these photographs. Also, the data leave no doubt that the pigmented gel coat does act as an effective barrier in keeping water out of the fiberglass laminate.

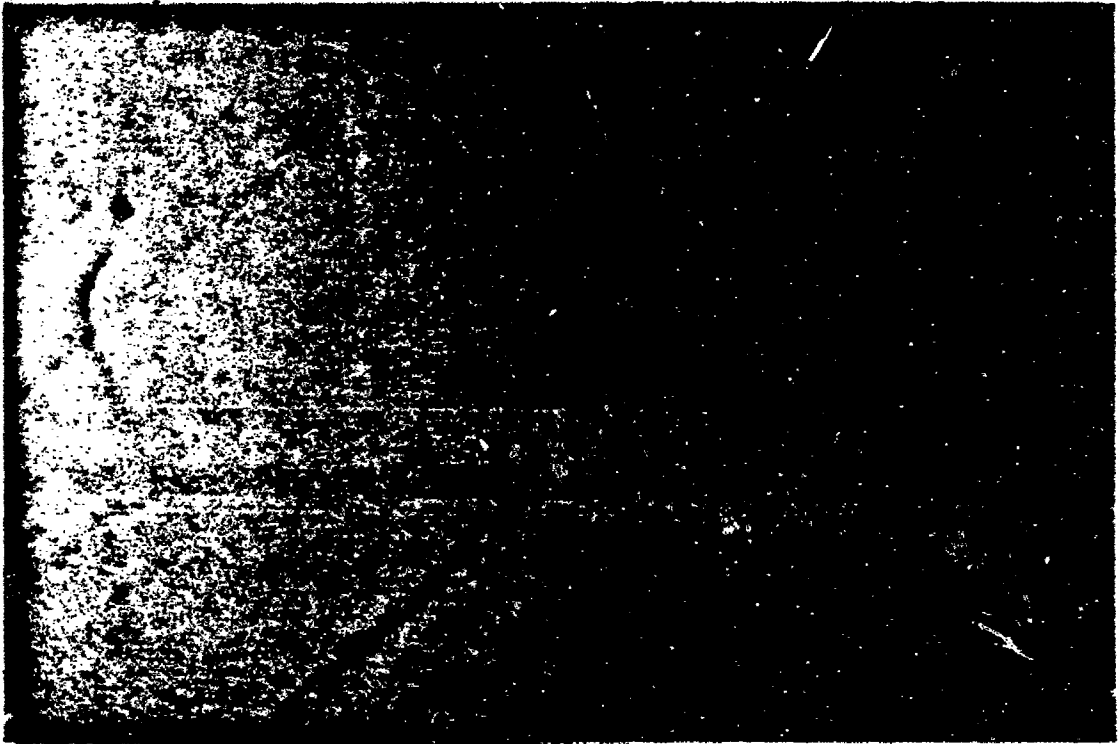
8. The X-layer, a Diffusional Interphase.

When an FRP structure is made up of layers, under certain circumstances, an unexpected layer forms between the different layers of the polyester structure. The new and unexpected layer is referred to as the X-layer because originally the reason for its existence was unknown. It is seen in boat hulls, in glass filled laboratory specimens and in non-reinforced polyester structures built up in layers.

The X-layer is about 0.1 mm (4 mils) thick. It is strongly birefringent when viewed under the microscope with polarized light (crossed nicols). The index of refraction of the layer is higher than the polyester above and below it thus proving that it has a different chemical composition than the surrounding polyester. Figure 16 shows two photomicrographs of the X-layer, one taken in white light and one with crossed-nicols. The birefringent interphase is always located at the bottom of the previously cured layer. The data below show that the layer is caused by diffusion of styrene monomer from the added wet layer into the cured polyester substrate.

Specimens were made using several different polyester resins, with and without glass reinforcement. The first layer, approximately 2 mm thick was cast onto a waxed glass surface. Additional layers were cast on top of the first layer after different times and under different conditions. When cured, the samples were cross sectioned using a diamond saw and polished to a thin section thickness of about 10 mils (.010"). These sections, perpendicular to the

a.)



b.)

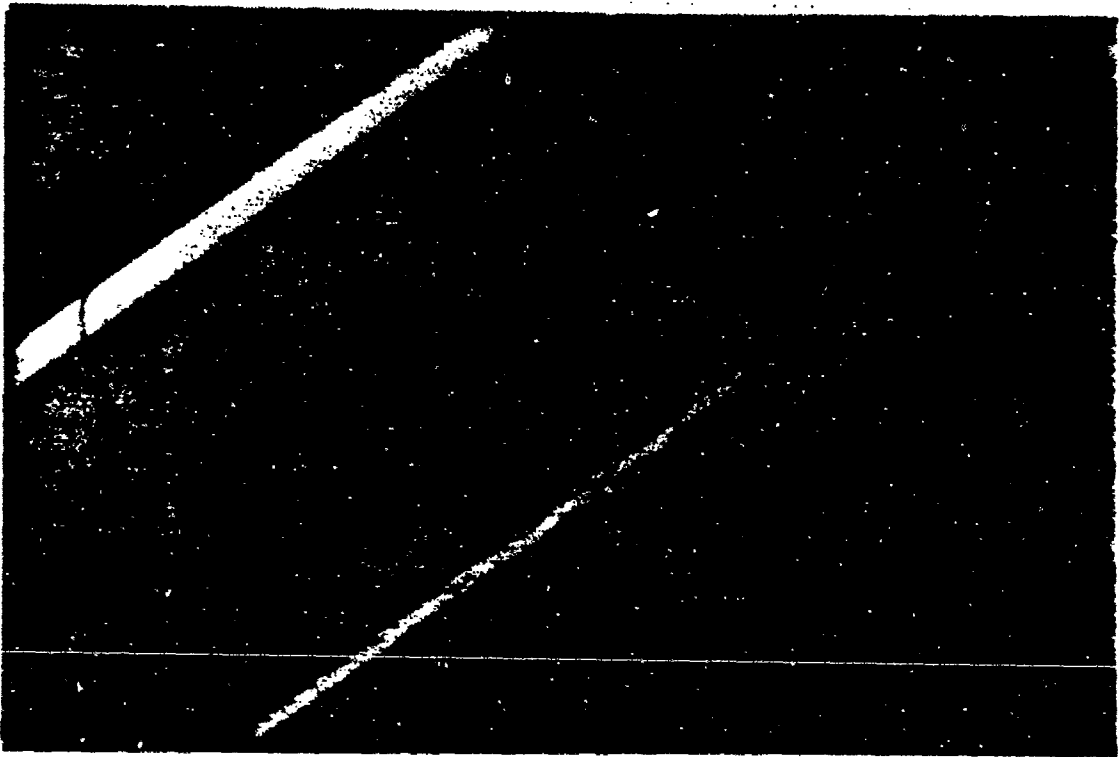


Figure 16. Photomicrograph of X-layer under a.) White Light b.) Polarized Light.

interfaces, were studied under the polarizing microscope. The x-layer thickness and degree of birefringence were measured. The following results were obtained:

1. When a single layer is cast no x-layer forms.
2. When a second layer is added to the first, before the first layer is completely cured, no x-layer forms.
3. When a second layer is cured on a fully cured first layer the x-layer interphase forms at the top of the first layer.
4. The x-layer is not related to air inhibition in the first layer. The first layer was covered with wax paper and allowed to cure before the wax paper was removed. The second layer was then cast and an x-layer, identical to the one formed in the matching experiment without the wax paper, formed.
5. A 1/4" thick by 1" x 1" polyester sample was cast and cured. Sectioning showed no x-layer. This piece was immersed in the identical resin liquid and the outer resin was then cured. Sectioning showed an x-layer at the top, bottom and sides of the immersed piece.
6. The top of layer I, adjacent to the x-layer interphase, shows a reduction of strain birefringence compared to the rest of the pre-cured layer. This suggests that styrene diffusion into the first layer has plasticized the zone adjacent to the x-layer. The thickness of the relaxed layer is close to the thickness of the x-layer.
7. There is, in most cases, some banding in the x-layer.
8. The thickness of the x-layer is independent of the first or second layer thicknesses.
9. Resins with a variety of styrene contents show essentially the same x-layer thickness.

All of the above observations can be explained by a diffusion of styrene monomer from the uncured added resin into the cured polyester. Styrene diffusion into polyesters is known to occur (3). As long as the added resin is uncured, styrene molecules are free to diffuse into the interstitial spaces of the pre-cured polyester first layer. As curing of the new resin proceeds, the monomer, styrene, will be converted to cross-linking units and diffusion will stop. The bottom of layer II will be depleted in styrene while the top layer I will be strained by the swelling produced by absorbed styrene. Diffusion into the solid polyester will be rate controlling (4). The sharp line between the styrene

saturated part of resin I and the remaining part of the resin indicate that diffusion is non-fickian in this case and a composition change at a well defined front exists. This front shows a sharp index of refraction change. Figure 17 is a sketch showing the x-layer. Dashed lines indicate the percent of styrene present at different points at different times. The exact styrene contents are not known but the estimates should be close. As suggested by the figure, after curing takes place, there is a possibility for back diffusion to occur.

The thickness of the x-layer depends on several factors. When the resin cures, the monomer is converted to polymer and there is no more free styrene to diffuse. The thickness of the x-layer is then set. Therefore anything that speeds up or slows down curing will affect the x-layer thickness. The higher the temperature, the faster the cure and the thinner the x-layer. More curing agent speeds up the set time and decreases the x-layer thickness. The degree of cross-linking of the pre-cured layer controls the rate of styrene diffusion into the precured layer and hence acts differently as a sink for styrene.

The banding observed in the interphase is due to several factors. More than one species can move from the liquid into the pre-cured material. In addition to styrene, catalyst molecules can also diffuse. Furthermore, back diffusion of styrene, after complete cure, can lead to substructures in the x-layer which appear as bands under microscopic examination. The full details of the diffusional interactions will be understood after more experimentation has been done. Further work needs to be done in this area.

The x-layer constitutes a property discontinuity in the material associated with the compositional and strain discontinuity. The sharp and strong birefringence is due to strain in the x-layer. This strain is caused by swelling of the previously cured polyester. The styrene depleted zone in the second layer also will be strained but to a lesser extent. The zone in front of the x-layer will be in tension.

The mechanical properties will also change in the x-layer. Figure 18 clearly shows a disk crack which initiated in the pre-cured layer. As it grew toward

Figure 17. STYRENE CONCENTRATION PROFILES IN THE REGION OF THE X-LAYER.

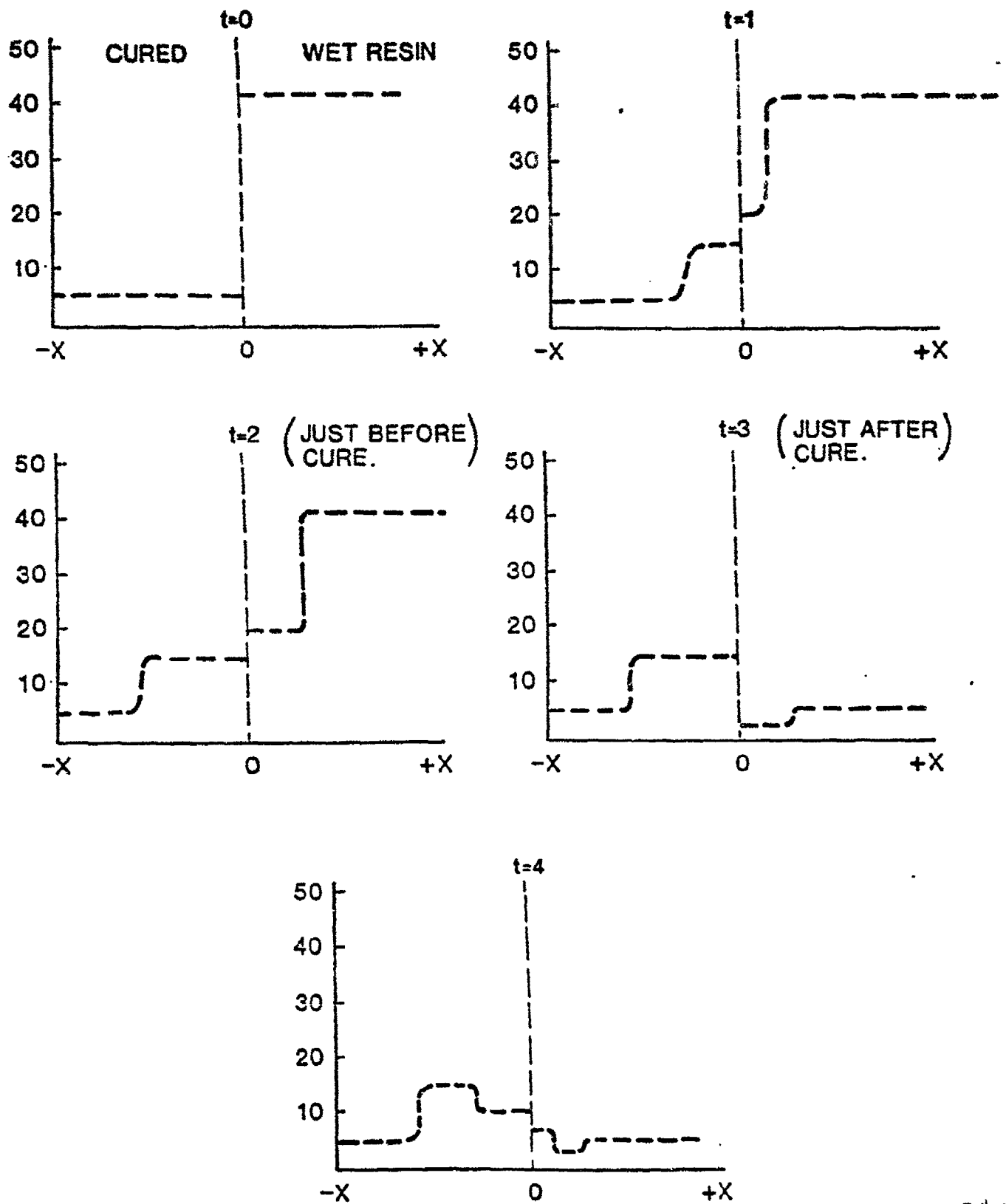




Figure 18. Photomicrograph Showing Disk Cracks which Initiated in the Pre-cured Layer and Were Deflected Along the X-layer, in a Glass Free, ISO-NPG/ISO Composite.

the x-layer it was deflected along the surface. This was observed in a glass free composite soaked in water at 65°C for many hours. The structure was free of cracks except in the tensile layer. None of these cracks spread through the x-layer.

An X-layer in a hull structure, could influence the location of blisters and could even promote hull delamination. The sharpness of the X-layer depends on how long a period of time elapses between fabricating different layers of the composite. The longer the elapsed time, the sharper the discontinuity becomes.

Because of the ease with which the X-layer can be located and observed, microscopic examinations of hull cross-sections can tell the observer at what points the hull construction was interrupted and generally how long a time elapsed between lay-up events. Continuous lay-ups are obviously the best practice. That way, no unexpected property change can occur in the laminate.

In one hull that showed delamination, the split occurred at an X-layer. If disk cracks formed on the gel coat side and were deflected at the X-layer, a cracking delamination could result. Also, the normal bending stresses and flexing stresses, which are applied to a hull by wave action, can be concentrated at an X-layer discontinuity which could also contribute to hull delamination. At this time, the data is not available to decide when an X-layer becomes a serious defect. Further studies need to be conducted on this phenomena.

The practice of curing a gel coat and then applying back-up resin can also produce an X-layer in the gel coat. Because gel coats are more flexible than laminating resin, the gel coat x-layer may not be a problem. The practice of continuing lay-up before the gel coat is completely cured is highly recommended. Some manufacturers wet a cured gel coat or laminate layer with styrene before continuing the lay-up process. This can weaken the structure more than is desirable, especially if too much styrene is used. It is virtually impossible to know the proper amount of styrene to use. Therefore, this practice should be discouraged and as continuous a lay-up schedule as possible should be used. Obviously more data is needed in this area.

9. Blister Initiation Time Distribution

The following study points out one of the problems in doing blister studies. Apparently identical samples do not blister at the same time and therefore a range of times must be given to describe blistering.

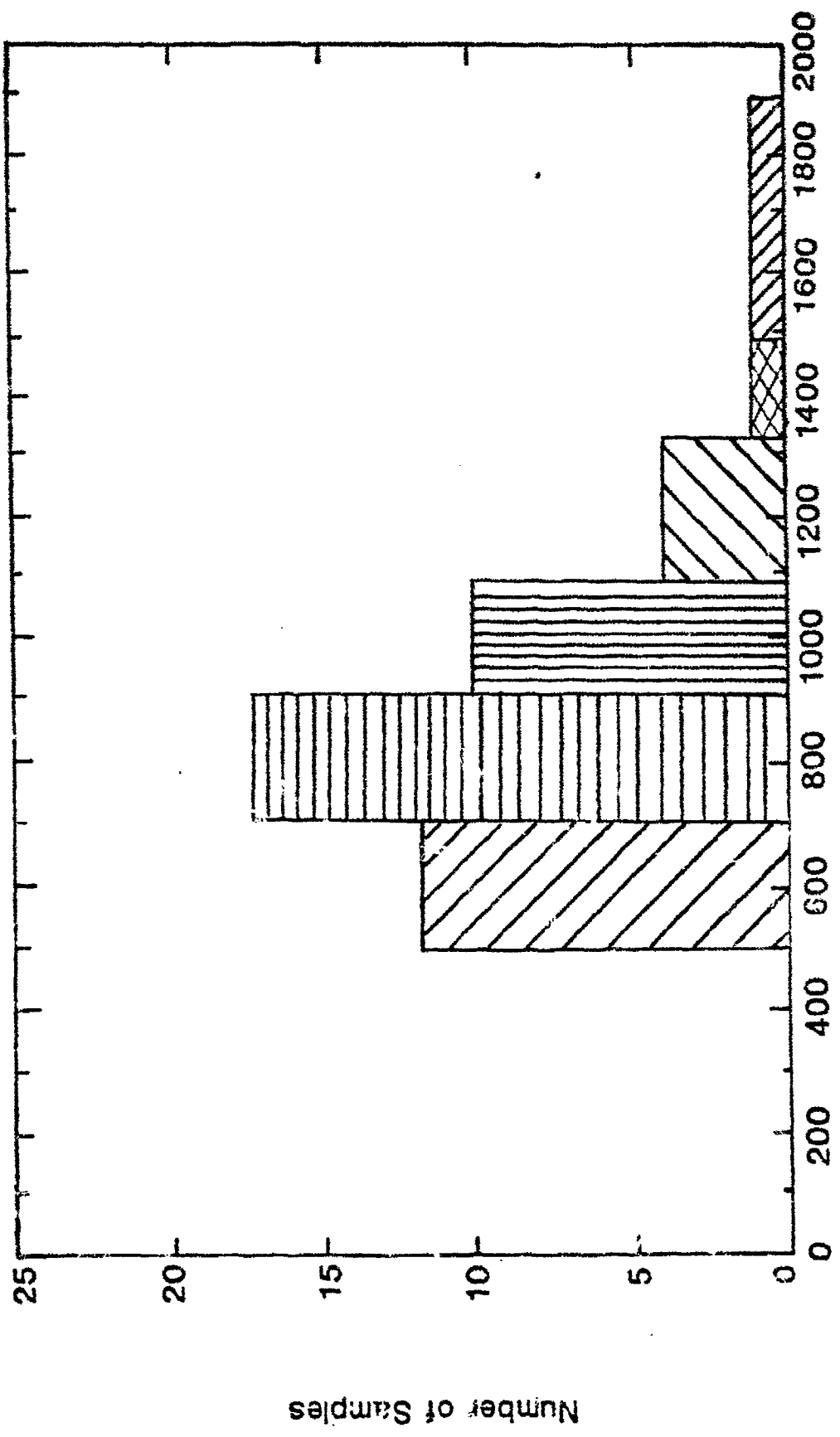
One very large panel (approximately 5' X 5') was constructed by a local boat manufacturer to be used for coating and repair technique evaluations. The panel is constructed of orthophthalic acid based laminating resin and gel coat. Three types of glass reinforcement were used in laminating: A skin coat, very lightly reinforced with chopped glass; veil region, lightly reinforced with a veil mat; and a heavily reinforced zone comprised of two layers of woven roving. The laminate was constructed and cured at ambient shop conditions. The panel was sawed up into more than 200, 4" X 4" samples.

A total of 72 samples were immersed at 65°C in a distilled water bath and allowed to blister. The samples were blistered so that they could be used later to help evaluate various coatings and blister repair techniques. Of the 72 samples, 45 were followed closely for blister initiation times.

A histogram of the distribution of blister initiation times of the 45 samples is shown in Figure 19. Assuming a normal distribution of the data, a mean of 970.7 hours (40.4 days), a median of 888.0 hours (37 days) and a variance of 235.6 hours (9.8 days) were calculated. For any normally distributed population, 99.74 percent of data will lie within three standard deviations of the mean. This means that 99.74% of all samples will blister between 264 and 1677 hours.

The discrepancy between the mean and median and Figure 19 clearly show that the data is slightly skewed to the right. However, the blister initiation times are close to a normal distribution.

80



Blister Initiation Time (hrs)

Figure 19. Distribution of blister initiation times for series 200

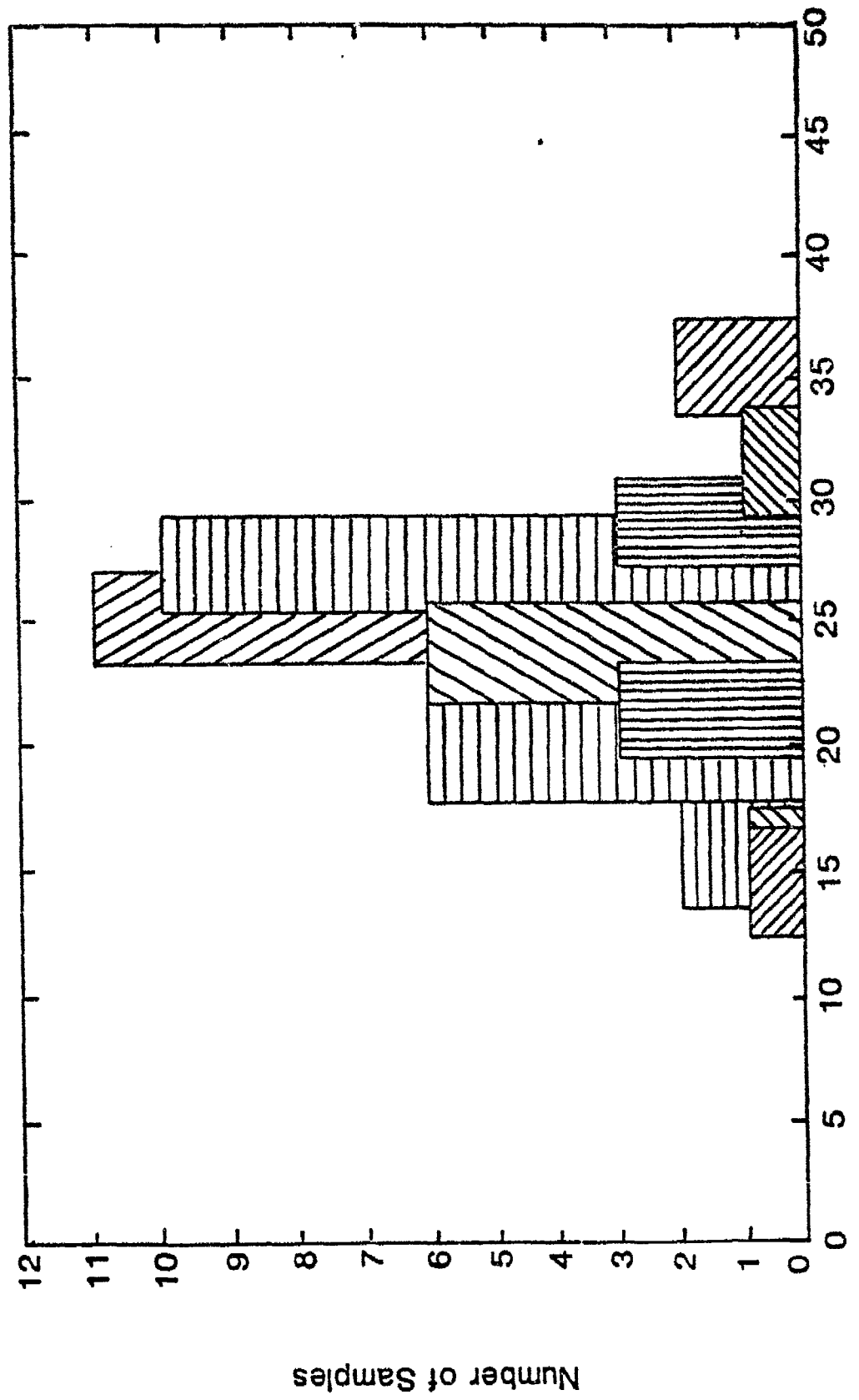
Both the skewness and broadness of the distribution can be explained mostly by variations in gel coat thickness and by the depth of the blisters' position.

The thickness of the gel coat was targeted between 20 and 25 mils. The gel coat was applied to a mold by an experienced operator using a spray gun. The thickness was spot checked using a mil gauge. Forty-five samples, to be used to test the performance of coatings over a gel coat, were measured for gel coat thicknesses. Five readings were taken for a samples and averaged. The distribution of the gel coat thicknesses is shown in Figure 20. The mean is 24.9 mils, median is 25.6 mils and the variance is 4.98 mils.

The broadness of the data clearly suggests the technique of spraying the gel coat, itself, assuming the thickness from experience and randomly spot checking the thickness does not yield a uniform thickness. Another factor is that the gel coat was sprayed onto a flat mold. Depending on the height of the operator, arm length and nozzle size, areas closer to the operator will be thicker than those farthest away from the operator. The spray becomes more disperse as it travels farther. This causes the thickness to be thinner farther away. The thickness data is skewed to the left. The most likely reason there are fewer samples with gel coat thickness greater than the median of 25.6 mils is that zones of overlap are at a minimum with an experienced operator, but are still unavoidable. Mold flatness and mold levelness could also play a role.

Gelcoat thickness is related to blister initiation time. The thicker the gelcoat, the longer it takes water to diffuse into the underlying laminate to initiate a blister. Figure 21 shows the relationship between blister initiation time and gel coat thickness for this set of samples.

Point 1 gives the blister initiation time for a blister formed just below the surface of a thin gel coat. Point 3 is the initiation time for a blister that formed 2-3 mm below a thick gel coat. The second point is the mean blister initiation time and mean gel coat thickness of all the samples. Using linear



Gel Coat Thickness (mils)

Figure 20. Gel coat thickness distribution for series 200

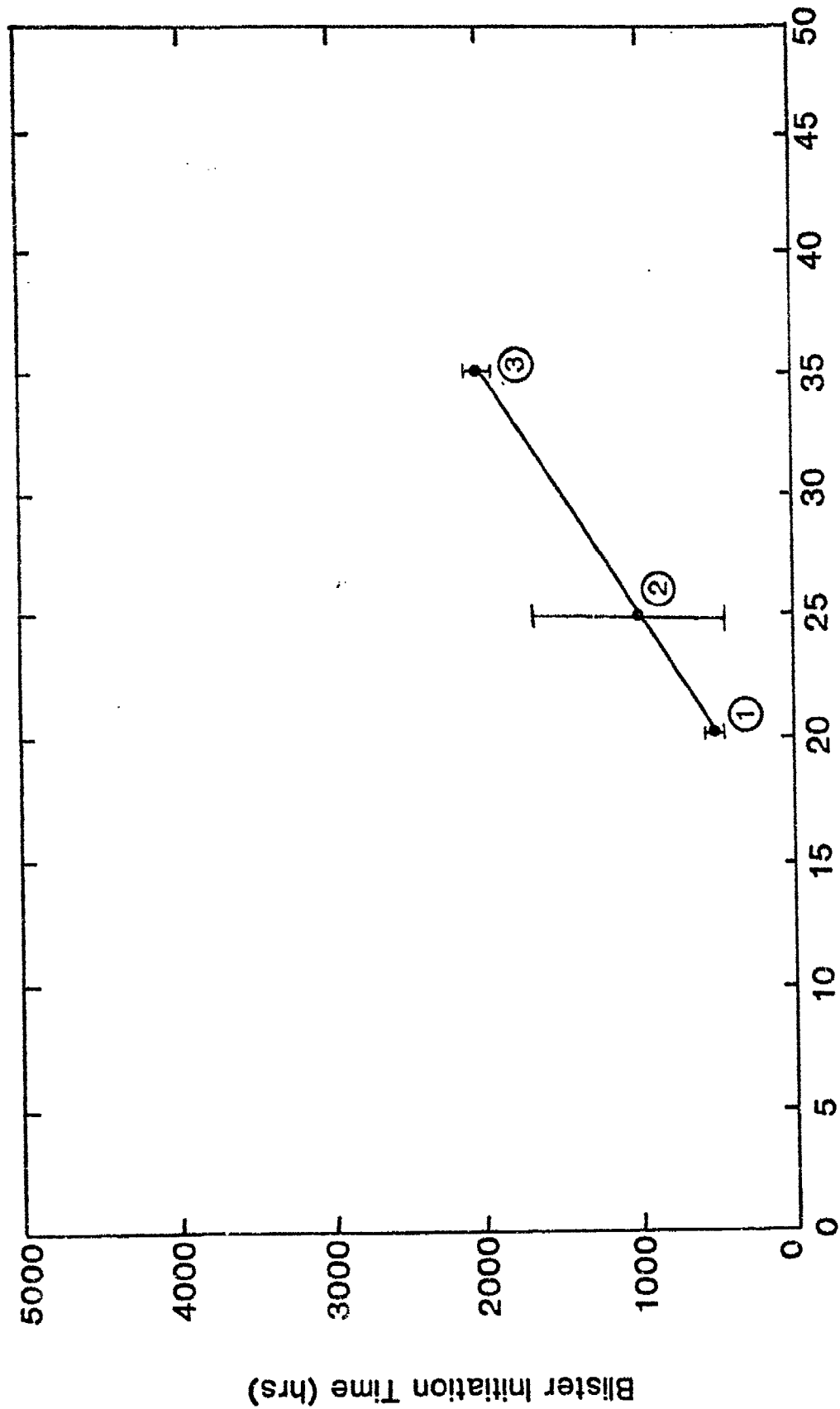


Figure 21. Blister initiation time vs. gel coat thickness for series 200

interpretation the following relationship is found:

$$B = -1556.58 + 102.5 \times T \quad (9.1)$$

Where B is the blister initiation time and T is the gel coat thickness

In the past it has been shown that if the gelcoat thickness is doubled, it takes roughly twice as long to initiate a blister. The line usually intersects the y-axis (blister initiation time) at a gel coat thickness close to zero.

The interpretation of this relationship can be given as follows:

It is true that blister initiation is a function of the distance water must travel through the gel coat to reach the laminate. However, for the above hypothesis to be true, that doubling the thickness roughly doubles blister initiation time, the blister must be positioned just beneath the gel coat. This is usually where most blisters are found. However, for this set of samples, most of the blisters occurred between the veil and woven roving regions, approximately 2-3 mm below the gel coat surface. The possible reasons for susceptibility to blistering and disk cracking in this zone is as follows:

1. The chopper glass reinforced zone is not susceptible to blistering. The chopped glass used is corrosion resistant and free of water soluble binder. The resin is eliminated as a source of blistering because the same resin was used at each stage of the lay-up process.
2. An x-layer is present between the chop and veil reinforced zones. The x-layer, as discussed in Section 8, has different properties than the surrounding resin and is under stress. A discontinuity in properties and stresses present potential sites for disk crack or any other type of crack formation.
3. An X-layer is an indicator of a discontinuous lay-up. Air inhibition layers, a source of water soluble materials, form with discontinuous lay-ups. Water soluble material is necessary for disk crack and blister

formation.

4. The veil glass and woven roving reinforced zones are subject to disk cracking and/or blistering because of the glass used or more probably because of the binders on the glass.

Because the laminate is susceptible to blistering at this distance beneath the surface, it means that the water had to diffuse in much more than the gel coat thickness before blisters could initiate. Although the thickness of the gel coat does matter, its effect would not be so apparent as if the blisters had formed just beneath the gel coat. Add to this the fact that there is also some variation in the chop layer thickness, the blister initiation time distribution is not as surprising.

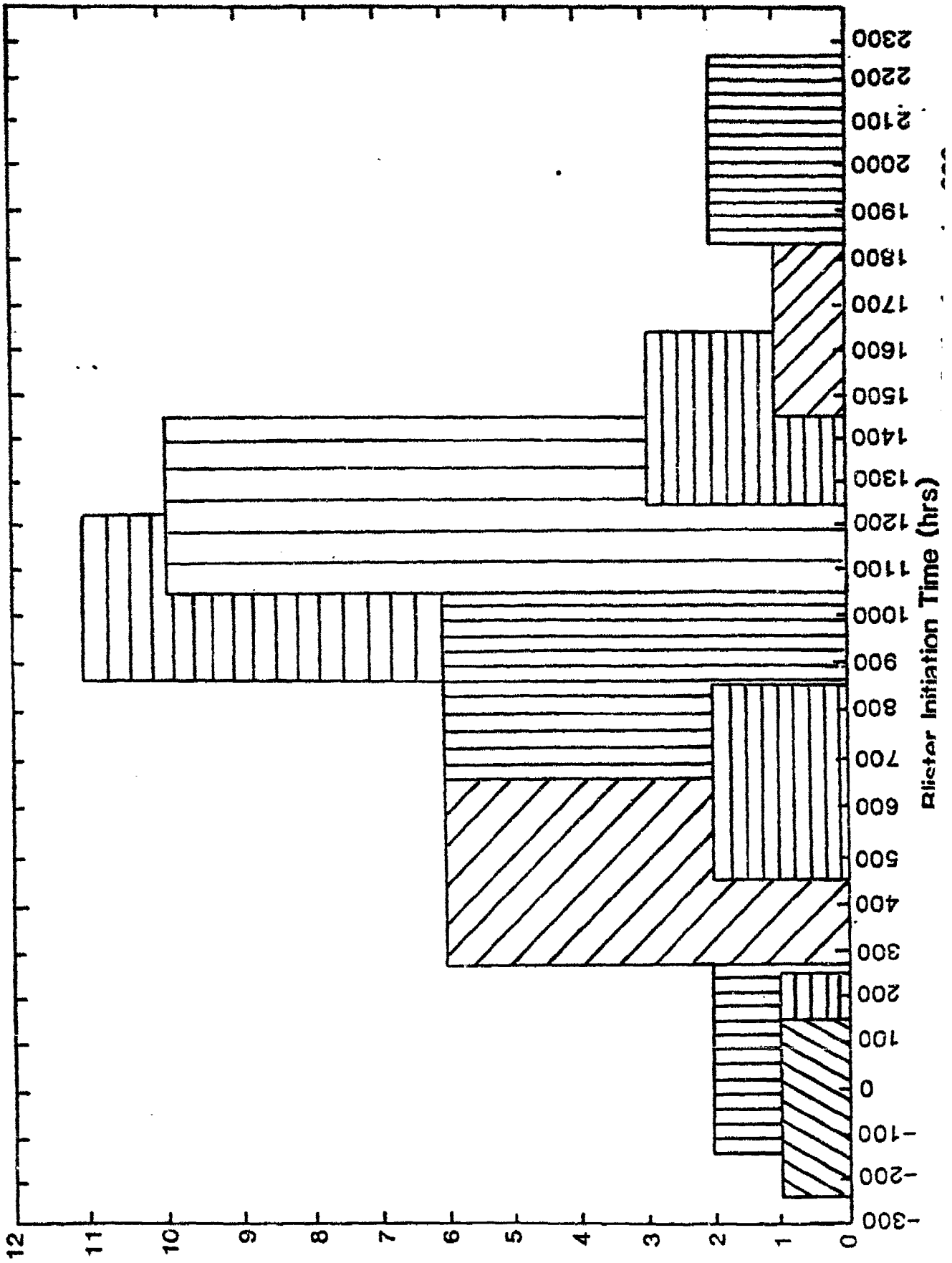
The added distance the water must travel would be reflected as a shift of the points to the right in Figure 21. This line also reflects problems in reporting blister initiation times. For the blisters that form deeper in the laminate, it is very difficult for these blisters to bulge outward. The blisters will tend to grow more parallel to the surface. For this reason the blisters cannot be seen on the gel coat surface until sufficient osmotic pressure has generated for it to grow outward. When these blisters are first noted they are usually very large. This means that the blister was hidden beneath the surface for some time before it was noted and therefore some of the blister initiation times reported are actually greater than the true values. Also, the thicker the gel coat the more difficult it is for a blister to bulge outward. This introduces an experimental error over which we have no control unless we destroy the sample. These factors are all taken into account in Fig. 21.

This line represents an average function of blister initiation time vs gel coat thickness for blisters that form just beneath the gel coat and those found 2-3 mm into the laminate. Using this relationship, the gel coat thickness data can be converted to blister initiation times and vice versa.

Figure 22 represents the result of converting figure 19 using equation (9.1). The width of the bars of the histogram represent the error in measuring gel coat thickness. The result is a mean of 979.2 hours, a median of 1066.9 hours and a variance of 476.5 hrs. Assuming a normal distribution, 99.74 percent of the data will lie between - 450.1 and 2498.6 hours. Though the distribution is very broad, the mean truly appears to be reflective of actual data which is 970.7 hours.

To conclude, the following explanations can be given to explain the distribution of blister initiation times in figure 19:

1. Variations in gel coat thickness are randomly distributed in the panel. This contributes significantly to the broad distribution of blister initiation times. Narrower distributions of gel coat thicknesses can be obtained in the laboratory but the techniques can not be used on boat hull. Thickness variations are inherent in the boat manufacturing process.
2. The deeper the blisters the longer water must travel to the site and therefore the longer it takes for a blister to initiate.
3. The deeper blisters do not show on the surface until some time after initiation and therefore the reported time is longer than the actual initiation time.
4. The blister initiating constituents in the laminating resin are randomly distributed.
5. Variations in glass concentration may affect blister initiation times. This may be a small contributor to the broadness and skewness of the data. Because glass acts as a heat sink, those areas with higher glass concentrations would develop lower exotherms and hence would cure less. Also, binder and/or coupling agent may be a source of water soluble material. Areas of heavier reinforcement would have a high concentration of water soluble material and therefore would blister faster. The glass also produces



stresses in the composite on shrinkage during cure and differential swelling during water absorption. These stresses would be greater in areas of heavier reinforcement. These areas would be more prone to disk cracking and hence blister initiation.

6. Thermal effects also may play a role. Areas that have thicker gel coat or laminating resin and lower glass concentration will develop greater exotherms and as a result will be more blister resistant. This may account for some of the skewness. Also, edges and corners of the mold would not be able to develop as high exotherms because of the added directions of cooling.

7. Most importantly, this data shows that, given all of the variables involved in manufacturing a boat hull and the materials used, it is impossible to predict, from laboratory specimens, an absolute time that a hull will blister. In order to predict boat hull blister initiation times, a very large set of samples must be constructed by methods similar to those used by boat manufacturers. This will give a distribution of blister initiation times that can be used to calculate the range of times in which blisters may initiate. Single sample studies are virtually meaningless for evaluating blister resistance.

This presents a problem in testing laboratory specimens as well. This study shows that to truly make a comparison between different materials, different lay-up procedures, etc., a large set of samples must be tested to find the range of the distribution of blister initiation times. Only if one distribution falls out of range of the other, can one specimen be said to be better or worse than the other.

8. Finally, data show that with an "identical" set of samples made by experienced professionals, a range of at least 700 hours can be expected in blister initiation times at 65°C. This means that two hulls, made by identical procedures, with the same materials, could show a difference of a year in blistering if they were continually immersed in warm water.

10. Blistering of Shop Prepared Samples

A frequent and valid criticism of many blister studies states that samples prepared in a laboratory environment are not comparable to samples prepared on the shop floor using standard industrial equipment. To address this question and to evaluate the effects of: 1. overcatalyzation, 2. undercatalyzation, 3. preparation at 50 to 60°F and 4. Construction with moistened fiberglass mats, four companies constructed panels using their standard manufacturing practice and commercially available materials. Then four additional panels, with the above deviations from standard practice, were made. The details of construction are given in table 3. The panels were cut into 4" X 4" test samples and supplied for testing.

The Coast Guard Office of Boating Safety designed the experiment, obtained the cooperation of the four companies and distributed the samples for testing. The four companies, whose valuable cooperation aided this study, were Hatteras Yachts, Cook Paint and Varnish Co., Coatings and Plastics, Inc. and Sea Ray Boats, Inc.

The samples, supplied to the University of Rhode Island, were tested by immersion in 65°C distilled water and the results are given in table 4. The studies were done blind. Only after performance was evaluated were the fabrication variables disclosed.

In several sets of samples a new water-composite interaction was discovered. This new type of blister will be referred to as "swelling blister". In one set of samples, with extremely thick gel coats, and in another set of epoxy coated samples, surface blisters were observed and assumed to be osmotic blisters, centered in the veil mat region. However, when these blisters were sectioned, no opening in the composite was found nor could any blister fluid be observed. Thin cross-sections were made through the samples and it was discovered that the blister resulted from a swelling of the surface material due to water up-take

Table 3. Details of Construction of Manufacturer Prepared Samples

GENERAL CONDITIONS	MANUFACTURER	SPECIAL CONDITIONS	SET DESIGNATION	GEL COAT MATERIAL USED	TARGET RESIN (WTS)	PER CENT C.C.	CURE TIME	APPLICATION BEFORE LAM.(MIN)	METHOD	CURE TIME(OP)	LAMINATING RESIN	PER CENT LAM. CATALYST	APPLICATION METHOD	SKIN COAT GLASS	LAMINATE REINFORCEMENT	LAM. CURE TIME (OP)	CURE TIME (HRS)
VARIED GEL COAT + LAM.	A	ST.	A-1	WHITE ISO/PC	22	1.5M	2.5	1.5M	PPS	85	ORTHODCPD	1.0M	SPRAY	2 oz + 4 oz	26 oz M.R. + 2 oz	85	24
VARIED GEL COAT	A	L.T.	A-2	S	S	2.0M	S	2.0M	S	50	S	1.2M	S	S	S	S	27
VARIED GEL COAT	A	U.C.	A-3	S	S	0.5M	10	0.5M	S	S	S	0.5M	S	S	S	50	72
VARIED GEL COAT	A	D.C.	A-4	S	S	1.0M	S	1.0M	S	S	S	5.0M	S	S	S	S	S
VARIED GEL COAT	A	MET	A-5	S	S	S	S	S	S	S	S	S	S	45-50% MOISTURE	S	S	S
VARIED LAM. ONLY	B	ST.	B-A	WHITE ISO/PC	38	1.8M	1	1.8M	PPS	77	ORTHODCPD	1.2M	ROLLER	C.G.	M.R. + C.G.	77	U.C.
VARIED LAM. ONLY	B	O.C.	B-B	S	S	S	S	S	S	S	S	6.0M	S	S	S	S	S
VARIED LAM. ONLY	B	U.C.	B-C	S	S	S	S	S	S	S	S	0.4M	S	S	S	S	S
VARIED LAM. ONLY	B	MET	B-D	S	S	S	S	S	S	S	S	S	S	76-37% MOISTURE	S	S	S
VARIED GEL COAT ONLY	B	L.T.	B-E	S	S	S	S	S	S	S	S	S	S	S	S	60	S
VARIED GEL COAT ONLY	C	ST.	C-1A	WHITE ISO/PC AND ALKYL VINYL ETHER	27	2.5M	0.5	2.5M	PPS	77	ORTHODCPD	2.5M	SPRAY	1.5 OZ	24/1.5 FAR MAT	77	U.C.
VARIED GEL COAT ONLY	C	O.C.	C-2A	S	S	1.2M	S	1.2M	S	S	S	S	S	S	S	S	S
VARIED GEL COAT ONLY	C	U.C.	C-3A	S	S	0.5M	S	0.5M	S	S	S	S	S	S	S	S	S
VARIED GEL COAT ONLY	C	MET	C-4A	S	S	S	S	S	S	S	S	S	S	MET 1.5 OZ	S	S	S
VARIED GEL COAT ONLY	C	L.T.	C-5A	S	S	S	S	S	S	S	S	S	S	S	S	53	S
VARIED GEL COAT AND LAM.	D	ST.	D-A	WHITE ORTHO/MPG	27	1.5M	1	1.5M	PPS	75	ORTHODCPD	1.5M	SPRAY	1.5 OZ	24 OZ M.R.	75	U.C.
VARIED GEL COAT AND LAM.	D	O.C.	D-B	S	S	0.5M	S	0.5M	S	S	S	4.5M	S	S	S	S	S
VARIED GEL COAT AND LAM.	D	U.C.	D-C	S	S	0.5M	S	0.5M	S	S	S	0.5M	S	S	S	S	S
VARIED GEL COAT AND LAM.	D	MET	D-D	S	S	S	S	S	S	S	S	S	S	MET 1.5 OZ	S	S	S
VARIED GEL COAT AND LAM.	D	L.T.	D-E	S	S	S	S	S	S	S	S	S	S	S	S	58	S
VARIED GEL COAT AND LAM.	D	C.G.	D-F	S	S	S	S	S	S	S	S	S	S	2 LAYERS C.G.	S	5	S

Abbreviation (alphabetical order):

- B = Benzoyl peroxide + 25 methyl aniline
- C.C. = Chopped Glass
- D.D. = Draw down
- ISO = Isophthalic acid based resin
- L.T. = Low Temperature
- M = Methylene ketone peroxide

- M.P.G. = Methylglycol
- O.C. = Over Catalyzed
- ORTHO = Orthophthalic anhydride
- P.C. = Propylene glycol
- P.P.S. = Pressure pot spray
- ST. = Standard conditions
- S = Same conditions as standard
- U.C. = Under catalyzed
- U.G. = Until gelled

MET = Glass was misted or steamed before use.
M.R. = Moore rating.

Table 4. Results of Blister Studies on F.R.P. Samples prepared by Manufacturers. Immersed at 65°C for 5240 - 5852 hours.

Mfg. Designation	Set #	Sample No.	Layup Variable	Gel Coat Blister thickness (mils)	Blister initiation time (hrs)	Density (blister/cm ²)	Maximum blister size (cm ²)	Swelling blisters	Sub-gel coat blisters
A	#1	1	S	30.0	104±61	20.5	0.2	+	+
A	#1	2	S	-	264±70	21.8	0.5	+	+
A	#2	1	LT.	32.0	264±70	8.5	0.2	+	0
A	#2	2	LT.	-	264±70	12.8	0.2	+	0
A	#3	1	UC	25.0	264±70	17.9	0.2	+	+
A	#3	2	UC	-	349±14	25.6	0.6	+	+
A	#4	1	OC	28.0	104±61	6.4	2.6	+	+
A	#4	2	OC	-	104±61	12.8	0.3	+	+
A	#5	1	W	31.0	264±70	18.6	2.9	+	+
A	#5	2	W	-	104±61	7.5	3.5	+	++
B	A	1	S	21.6	-	0	-	0	++
B	A	2	S	19.7	-	0	-	0	0
B	B	1	OC	21.6	-	0	-	0	0
B	B	2	OC	21.6	-	0	-	0	0
B	C	1	UC	23.6	-	0	-	0	0
B	C	2	UC	18.9	-	0	-	0	0
B	D	1	W	21.6	-	0	-	0	0
B	D	2	W	23.6	-	0	-	0	0
B	E	1	LT	21.6	-	0	-	0	0
B	E	2	LT	22.4	-	0	-	0	0
C	1A	1	S	30.0	171±24	5.4	1.6	0	++
C	1A	2	S	-	228±14	6.9	1.0	0	++
C	2A	1	OC	28.0	279±37	23.0	0.3	+	0
C	2A	2	OC	-	279±37	19.2	0.4	+	0
C	3A	1	UC	36.0	205±10	0.6	1.8	0	++
C	3A	2	UC	-	349±33	1.9	2.2	0	++
C	4A	1	W	30.0	108±58	2.2	1.3	+	++
C	4A	2	W	-	108±58	3.4	0.6	+	++
C	5A	1	LT	26.0	228±14	4.3	1.1	+	+
C	5A	2	LT	-	349±33	6.7	1.0	+	+
D	A	1	S	42.0	589±59	3.7	1.7	+	+
D	A	2	S	-	589±59	2.1	1.5	+	+
D	B	1	OC	36.0	446±35	11.8	1.7	+	+
D	B	2	OC	-	446±35	8.3	1.9	+	+
D	C	1	UC	33.0	397±13	10.9	0.4	+	+
D	C	2	UC	-	518±11	4.8	0.5	+	++
D	D	1	W	38.0	446±35	3.5	1.3	0	++
D	D	2	W	-	446±35	6.7	1.4	0	++
D	E	1	LT	41.0	446±35	9.1	2.4	0	+
D	E	2	LT	-	397±13	5.3	0.9	0	+
D	F	1	CG	33.0	446±35	6.4	0.3	+	+
D	F	2	CG	-	1127±219	9.1	0.2	+	+

Abbreviation:

L.T - Low Temperature

O.C - Over Catalyzed Gel Coat, Laminate or Both

0 - None

+ - Present, but not wide spread

++ - Wide spread

S - Standard method

UC - Under catalyzed

W - Wet

CG - Chopped glass

at certain spots as shown in figure 23 a.

This observation constitutes a problem in data taking. Without some destructive test, it has been impossible for us to differentiate an osmotic blister from a swelling blister. The sample must be drilled or sectioned before the distinction can be made. Preliminary determinations suggest that a non-destructive ultra-sonic test could differentiate the two.

In certain samples, swelling blisters nucleated osmotic blisters inside the gel coat. As the swollen zone pushes against the surrounding gel coat it produces an upward thrust similar to plate buckling. This causes a crack under the gel coat and initiates osmosis. The blister void is small and saucer shaped and spreads to the surface causing a semi-circular crack around part of the swelling blister. This type of swelling is often related to the formation of a surface waviness which is commonly seen on gel coats prior to the onset of blistering. It is the same process, on a much less dramatic scale, as the swelling described by Tanaka et al. (5).

One type of swelling blister observed in epoxy coated composites was caused by sanding debris included in the surface coating. When a multi-layer system is used to repair a blistered hull, two layers of a clear penetrating or sealing epoxy are painted on the surface. Each layer must be sanded before the colored surface layer is built up. The sanding promotes mechanical adhesion and removes a "blush" or tacky air inhibited layer. Because the particles are sticky they can adhere to the surface and be incorporated into the next layer. Sectioned swelling blisters of an epoxy coating showed clusters of clear particles in the surface layer at the center of the swelling blister. No internal crack or blister fluid was present in these cases. No such particles are observed in the swelling blisters in gel coats and it is assumed that the swelling begins at a slightly undercured zone. In this report some of the blisters observed are swelling blisters. However, in the tables, no effort has been made to differentiate between the two types of blisters when initiation times are reported. If swelling blisters were found by sectioning their occurrence is noted in the tables.

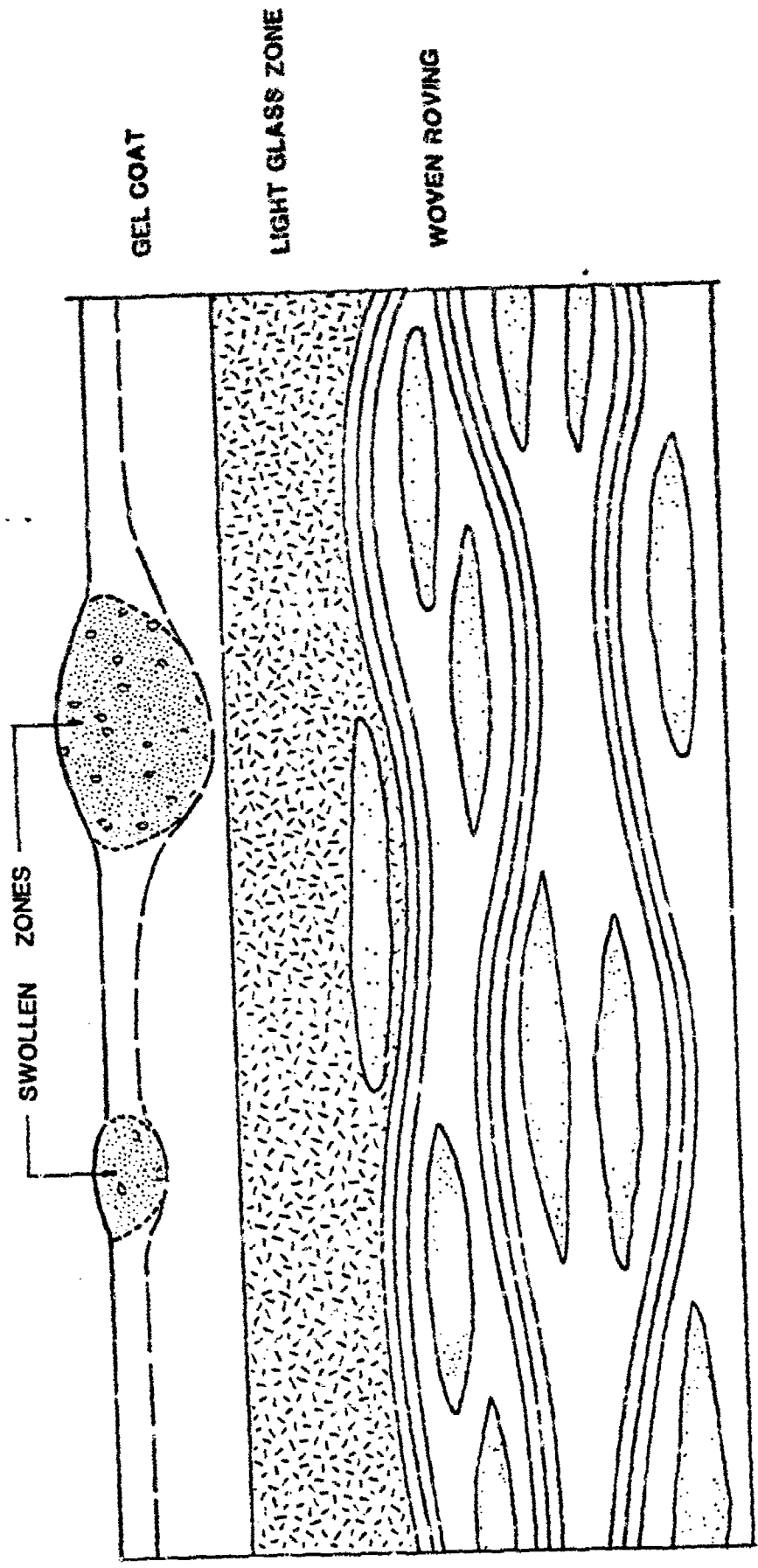


figure 23a Schematic diagram showing swelling blisters in a gel coat. The dotted line represents the water diffusion front.

In addition to swelling blisters, the more frequently encountered sub-gel coat blisters are also observed. Since the location and type of blister can not be determined until the samples are sectioned at the end of the tests, the initiation time refers to the first observed blisters (which will be swelling blisters if they form on a given sample). Swelling blisters tend to form in thick gel coats. Hence the surprising result that blisters initiate in very short times, even with thick gel coats, is contrary to the rule of thumb that gel coat blistering initiation times are a function of gel coat thickness. Figure 23 b and c shows samples A-1-1 which has only swelling blisters, many of which cracked on drying, and sample C-5-A1 which has sub-gel coat blisters.

A thorough review of the data on Table 4 leads to the following conclusion:

1. Too many simultaneous variables were used and therefore, absolute results and some factors cannot be drawn.
2. Set B data show that in certain cases, the gel coat determined the behavior of the laminate regardless of multiple variable changes.
3. Sets A and B show that identical gel coat materials, used by two different manufacturers, gave substantially different results.
4. Low temperature fabrication did not seriously affect the blister resistance.
5. Swelling blisters occurred on many samples. Overcatalyzation produced them on one set, where the standard was free from them.
6. Swelling blisters occur more commonly in thick gel coats.
7. Wet glass produces large blisters.
8. Iso/PG based gel coats performed as well, if not better than, neopentyl glycol containing material.
9. The data indicates, but does not prove, that a wide variation in the percent of catalyst used did not affect the results. There is evidence to suggest that gel coats should be catalyzed with at least 1.8 percent MEKP when that catalyst is used.
10. The blister free panels were prepared under laboratory conditions and were much smaller in size than the panels prepared by the three manufacturers (96 square inches vs 600 square inches).

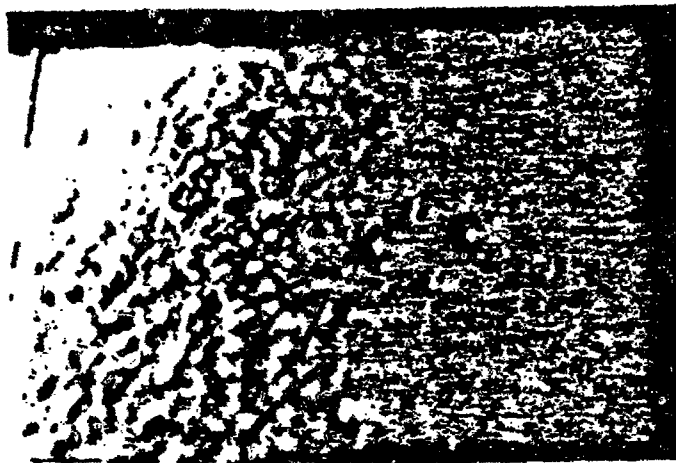


Figure 23b. Gel Coat Swelling Blisters, Viewed from the Surface, on Sample A-1-1.



Figure 23c. Sub-Gel Coat Blisters, Viewed from the Surface, on Sample C-5-A1.

11. Water Diffusion Profiles in Coated and Uncoated F.R.P.

Computer software has been developed at the University of Rhode Island that is able to model the moisture content in a multi-layer laminate at any depth as a function of time. The programs are based on the assumption that Ficks' laws of diffusion holds for the samples. Many studies have shown this to be a valid assumption.

In an attempt to determine the effectiveness of a typical epoxy based coating system in keeping moisture out of a hull, six different cases, all at 28°C, were studied using this computer software; Case 1 - laminate with a 20 mil orthophthalic acid based polyester gel coat over the same laminating resin, exposed to water for 200 hours; Case 2 - same as Case 1, except 4000 hours exposure to water; Case 3 - in place of a 20 mil gel coat, a 10 mil epoxy coating is used and the sample is exposed for 200 hours; Case 4 - same as Case 3, except exposed in water for 4000 hours; Case 5 - 10 mils of epoxy over a 20 mil gel coat exposed for 200 hours; Case 6 - 10 mils of epoxy underneath a 20 mil gel coat exposed for 200 hours.

Only the front side of each sample was assumed to be exposed to water at 28.5°C. The back side of each sample is assumed to see ambient conditions of 70 percent relative humidity and 28.5°C. The best available diffusion coefficients are assigned to each layer after the thickness is entered. The computer solves the diffusion equations for the times assigned and prints out the diffusion profile.

Results are presented in figures 24 to 29. Comparing the results after 200 hours of immersion, it is seen that using 10 mils of epoxy in place of a gel coat can reduce the water content at the coating, back-up resin interface, by almost half. Using an epoxy coating, over or underneath a gel coat, will allow almost no moisture into the laminate in 200 hours. After 3000 - 4000 hours of immersion in water, with or without an epoxy coating, the sample becomes almost totally saturated with water.

Figure 24. Water Concentration Profile in Case 1 Composite. 200 hours at 28.5 °C. Isophthalic Gel Coat on Orthophthalic Resin.

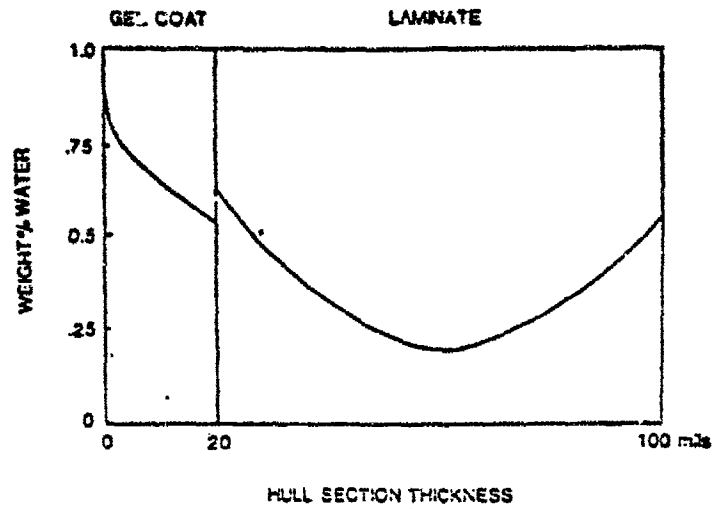


Figure 25. Water Concentration Profile in Case 2. 4000 hours at 28.5°C. Iso Gel Coat on Ortho Resin .

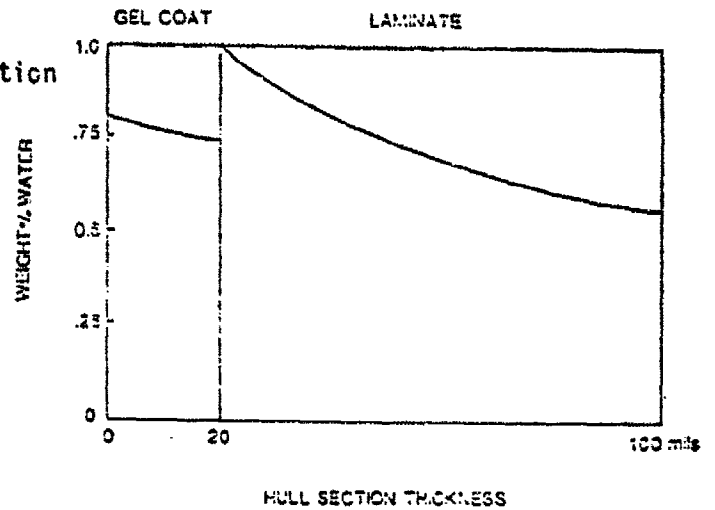


Figure 26. Water Concentration Profile in Case 3 Composite. 200 hours at 28.5°C. Epoxy Coating on Ortho Resin.

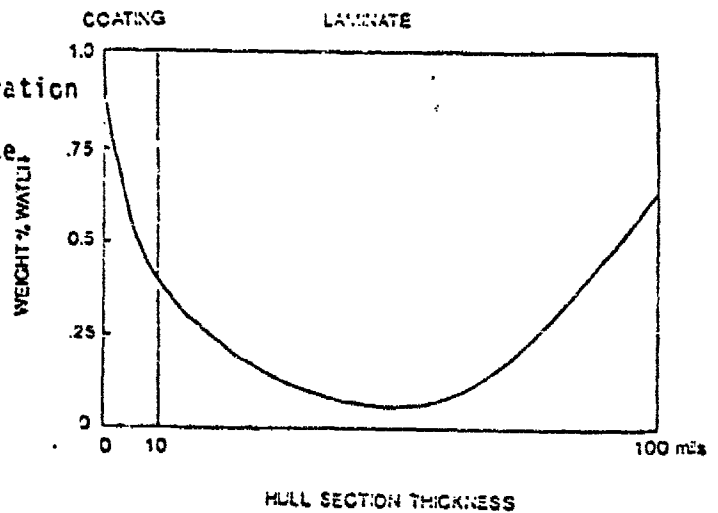


Figure 27. Water Concentration Profile in Case 4. 4000 hours at 28.5°C. Epoxy Coating on Ortho Resin.

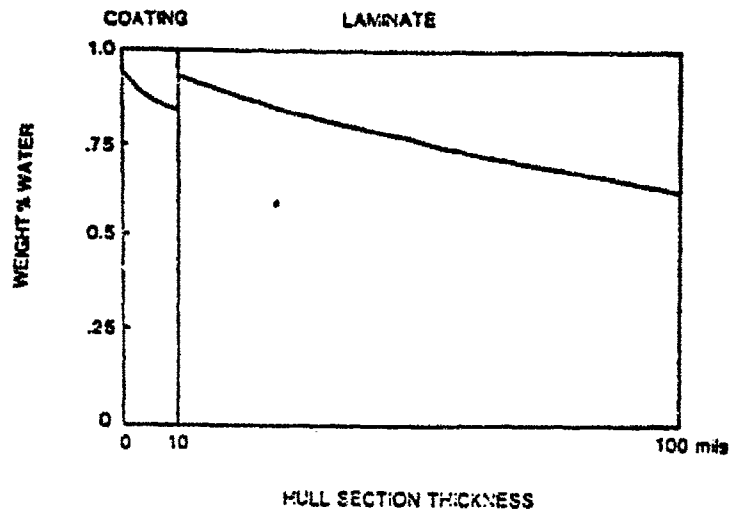


Figure 28. Water Concentration Profile in Case 5 Composite. 200 hours at 23.5°C. Epoxy Coating, over Iso Gel Coat, on Ortho Resin.

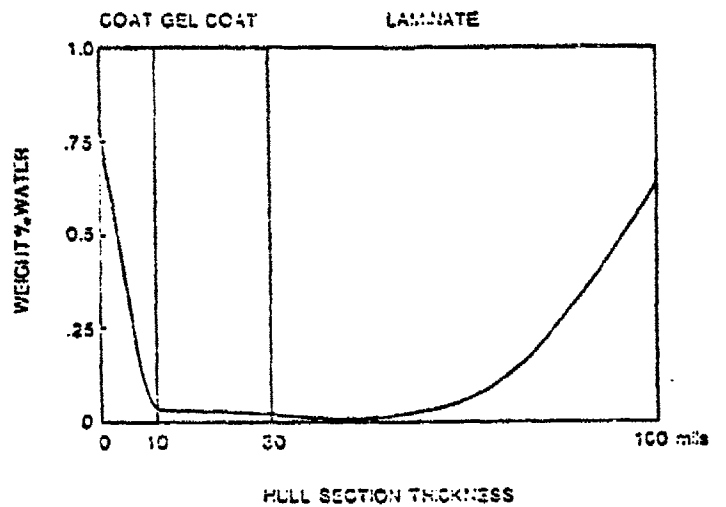
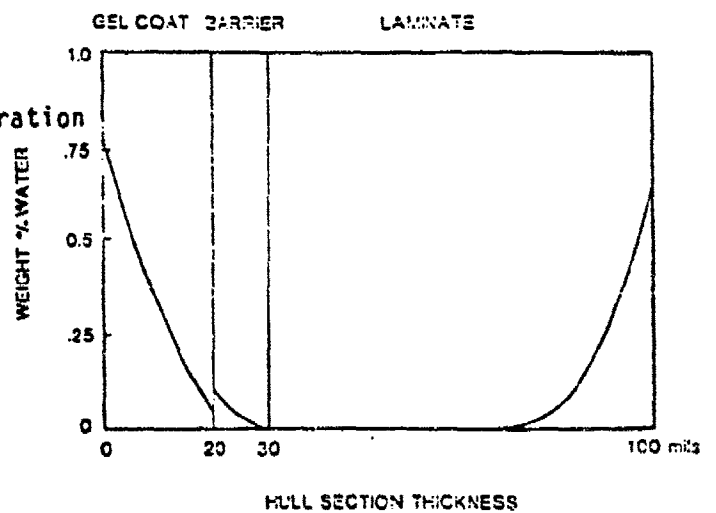


Figure 29. Water Concentration Profile in Case 6 Composite. 200 hours at 28.5°C. Epoxy Coating, under Iso Gel Coat, on Ortho Resin



From these results it is concluded that an epoxy coating will perform far better than a gel coat in keeping moisture out of a hull initially. However, after prolonged exposure to water, even an epoxy coating will allow the hull to saturate with water.

These water profiles are for continuous storage of a boat in water at the temperature given (28.5°C - 88°F - very warm water). If the average water temperature is much lower, then saturation will take longer--roughly double the time for each 10°C or 18°F. Further, if the boat is stored on land during the winter months, diffusion of water will reverse. Hull saturation may never take place in boats that are land stored many months each year, provided the bilge is kept dry and well ventilated.

Other factors, such as the bond and the stresses developed at the back-up resin coating interface, play an important role in determining the performance of a coating system. These factors, which may even alter the diffusion of water through the laminate, have not been taken into account in this computer software. Also, the role of fillers and glass reinforcement have not been considered. Interaction effects between water and the polymers and between coatings and the polymers are also ignored for this model. They are important and these graphs should be used as a comparative indication of the role of coatings in retarding water pick-up by laminates.

The 200 hour profiles shown in figures 26 and 28 draw attention to an important point regarding water diffusion. Diffusing water molecules enter a polymer from a surrounding medium any time the partial pressure of water is greater in the medium than it is in the polymer. If the surrounding medium is air, containing some water, i.e. at some relative humidity, and the polymer is dry, water molecules will leave the air and diffuse into the polymer. When the water concentration in the polymer reaches an equilibrium level, diffusion stops. In 100 percent relative humidity air, the water level in the polymer is identical to the water level obtained by immersing the polymer in liquid water. It is clear then that the hull picks up water from the inside of the hull as well as from the outside.

Providing the relative humidity of the air stays below 100 percent, for long periods, inner water absorption is not a problem. With time, a steady state gradient of water will exist from saturation at the gel coat side, to some lower value set by the amount of water in the air at the back side.

It has been established that disk cracks can only form in a polyester resin if the resin first reaches saturation. Disk cracks initiate blistering and osmotic cracking. If the backside of the resin reaches saturation, disk cracks will form throughout the hull thickness. Blisters or osmotic cracks will then form, leading to delamination and hull damage.

If water builds up in the bilge and stays there for prolonged periods, the hull will saturate and disk cracks will form. A relatively dry inner hull will prevent deep damage. The conclusions are inescapable. Bilge dryness will preserve the long term life of the hull. It is impossible to keep water out a of hull. However, if the bilge is designed for effective water removal and provisions are made for air circulation, the inner hull should be protected from water damage indefinitely. For these reasons and because of the severe leaching damage caused by free water on the inside of the hull (discussed in section 7), bilge dryness and ventilation is critical.

12. Drying of the Hull Prior to Repair

A series of drying studies were conducted for two reasons. Recommendations for boat repair must include a drying schedule for a hull. Also, for our tests on repair techniques, a drying procedure had to be established.

After the gel coat has been removed from a badly blistered hull and the surface has been thoroughly washed, the boat must be dried before repair can begin. Guidelines have been developed from our experiments on drying rates, diffusion coefficients and saturation experiments.

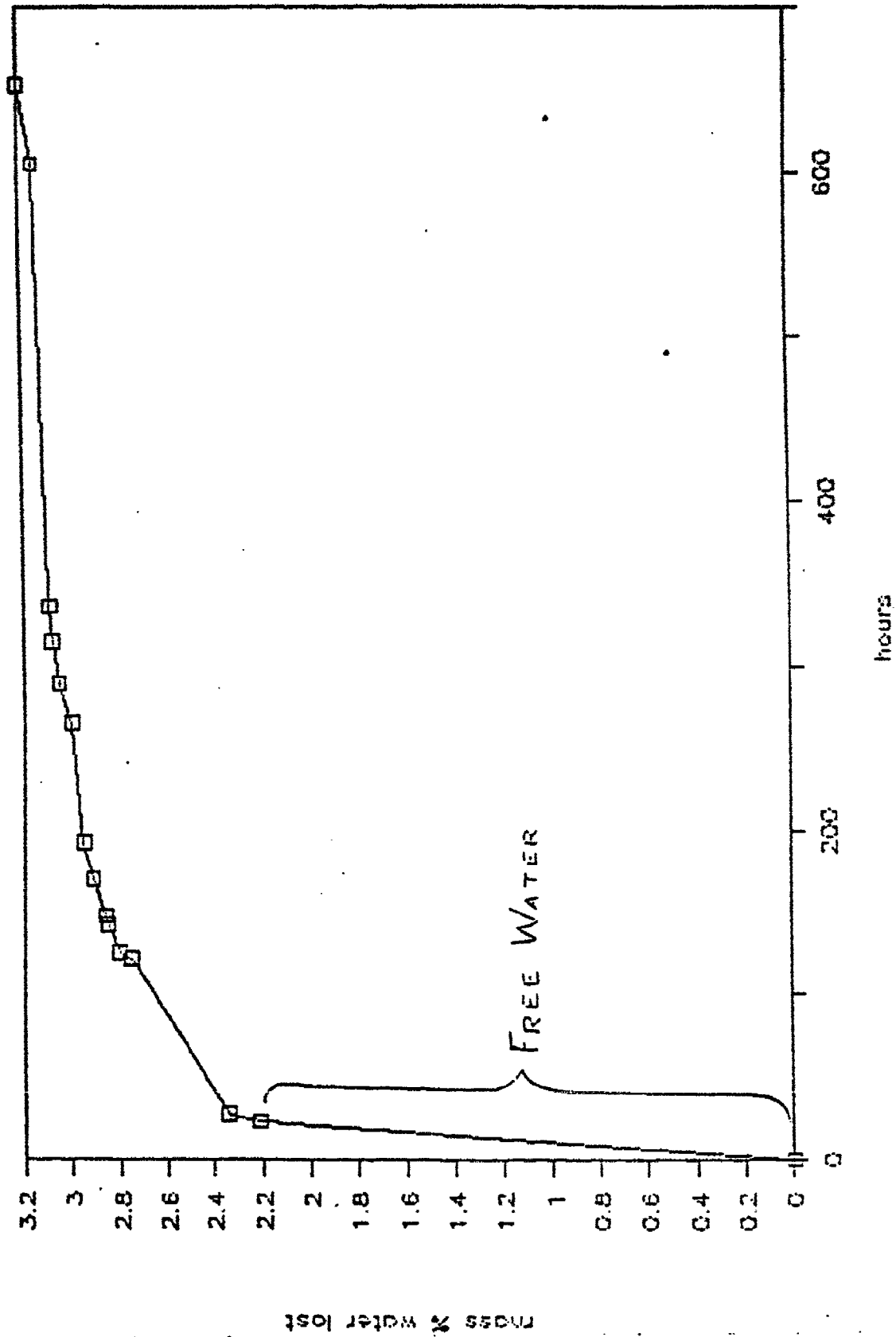
A boat hull, which had blistered in use, was cut up with a saw into small panels. The panels were soaked in water for several weeks and then repaired as described in section 14 of this report. Before repair could begin, the drying characteristics of the hull material had to be evaluated. Some panels were backed with a core material which held free water. During drying, the free surface water evaporates very quickly. This gives a high initial slope to the drying curve. Following that initial drying, the hull material then dries by diffusion of absorbed water out of the hull structure. As shown in figure 30, when the free water is subtracted from the water loss, it contains about 1 percent water. It takes hundreds of hours to reach total dryness. Data on twenty other sections confirms the total absorbed hull water to be equal to about 1 percent and the total drying time, even in a forced convection drying oven, at 65°C, is in the order of 300 hours.

In practice, removal of all the water from the hull would be impossible. If the water content is brought below 0.5 percent by weight, the reoccurrence of blisters will be significantly delayed. The difficult problems for the repairer is knowing how long drying should take place in order to reach a water content of 0.5 percent. There are several procedures which can be considered.

12.1 Moisture meters

A moisture meter applies a radio frequency field to the area being studied. This field is nondestructive. The moisture content is measured by electronically assessing a change in capacitance. The capacitance of the hull depends on the dielectric constant of the hull material. For a given frequency the capacitance is some function of water content. The meter uses two scales: Scale A, for use with polymers, including boat materials, and less dense materials and scale B, for use with materials such as brick, stone and concrete.

Figure 30. natural drying of laminate



Moisture meters reading are not absolute values of moisture content and must be used with extreme care. Two moisture meters were obtained and tested. Two saturated laminates were dried in a circulating oven at 150°F till dry. Weight and moisture meter readings, using both meters, were taken periodically. Results are given in Figure 31, showing weight percent water measured using both moisture meters vs the actual weight percent of water inside the laminate. It can be seen that there are no apparent differences between the two moisture meters.

In an attempt to calibrate the moisture meter for hull materials, two different samples were studied; a sample with a gelcoat and a sample without a gel coat. The sample with a gelcoat was immersed in water at 65°C for approximately one month and then soaked in cold water. The sample with no gel coat was placed in water at 65°C for one week. Both samples were saturated. They were then oven dried in a circulating oven at 65°C. Weight and moisture meter readings, using scales A and B, were taken periodically until they were completely dried. The data is given in figures 32 through 35.

Although both scales respond to changes in moisture content, the reading must be calibrated to obtain a moisture content. scale A is more sensitive to changes in moisture content while the reading on scale B are closer to actual moisture values especially in the latter stages of drying.

Data measured on the rate of drying indicates that both the scales drop off quickly at early stages of drying. During drying, the surface dries first and the interior dries after a longer time. Since meter values dropped off quickly initially, this suggests that surface moisture has the largest effect. Readings on scale B did not drop off as quickly as for scale A, for either sample, which suggests that scale B applies a field which penetrates the sample more deeply than scale A. Scale B duplicates the actual moisture content much more closely than does scale A, especially after the sample is partially dried.

Figure 31.—moisture meter calibration

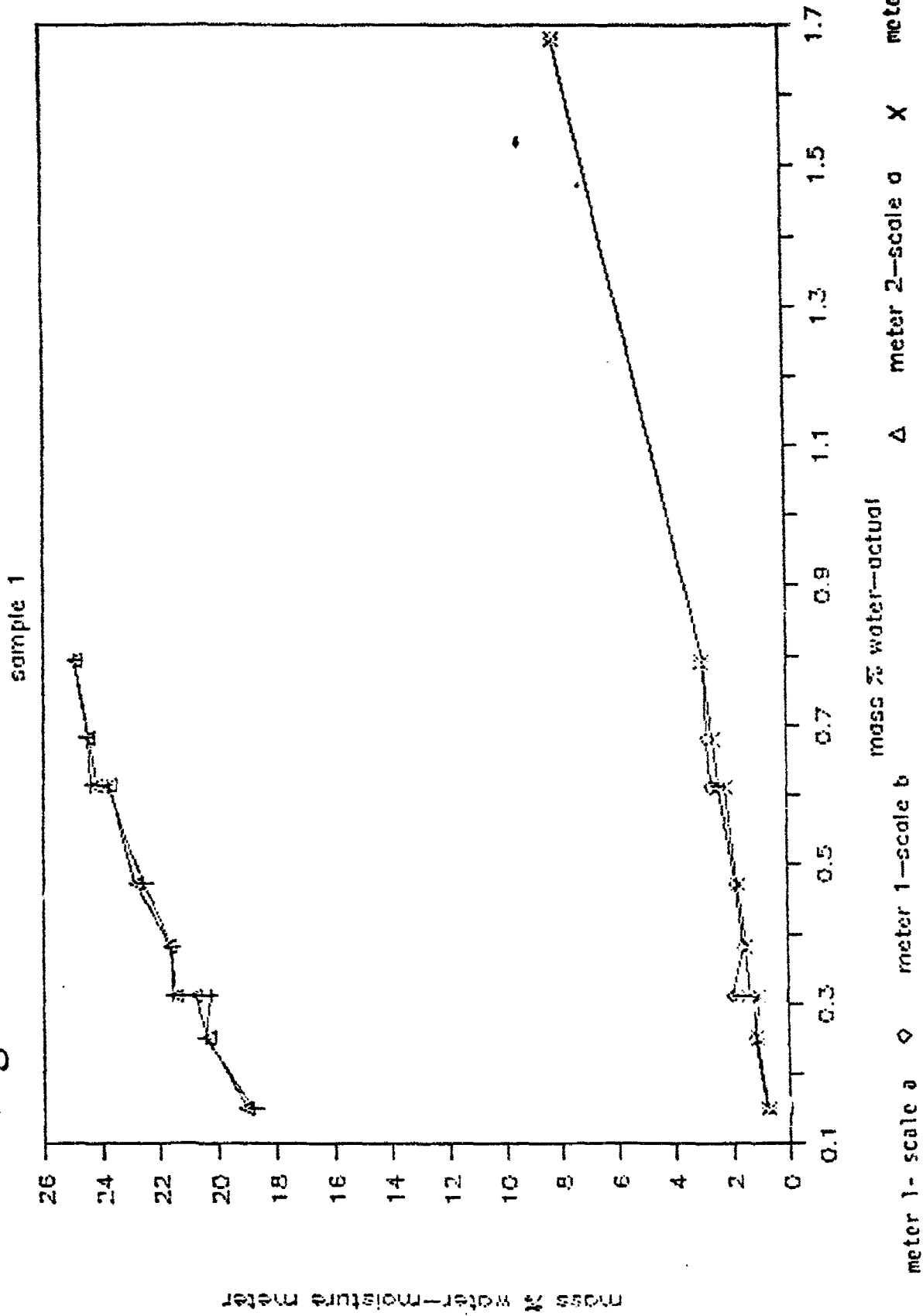


Figure 32. -moisture meter calibration
(no gel coat)

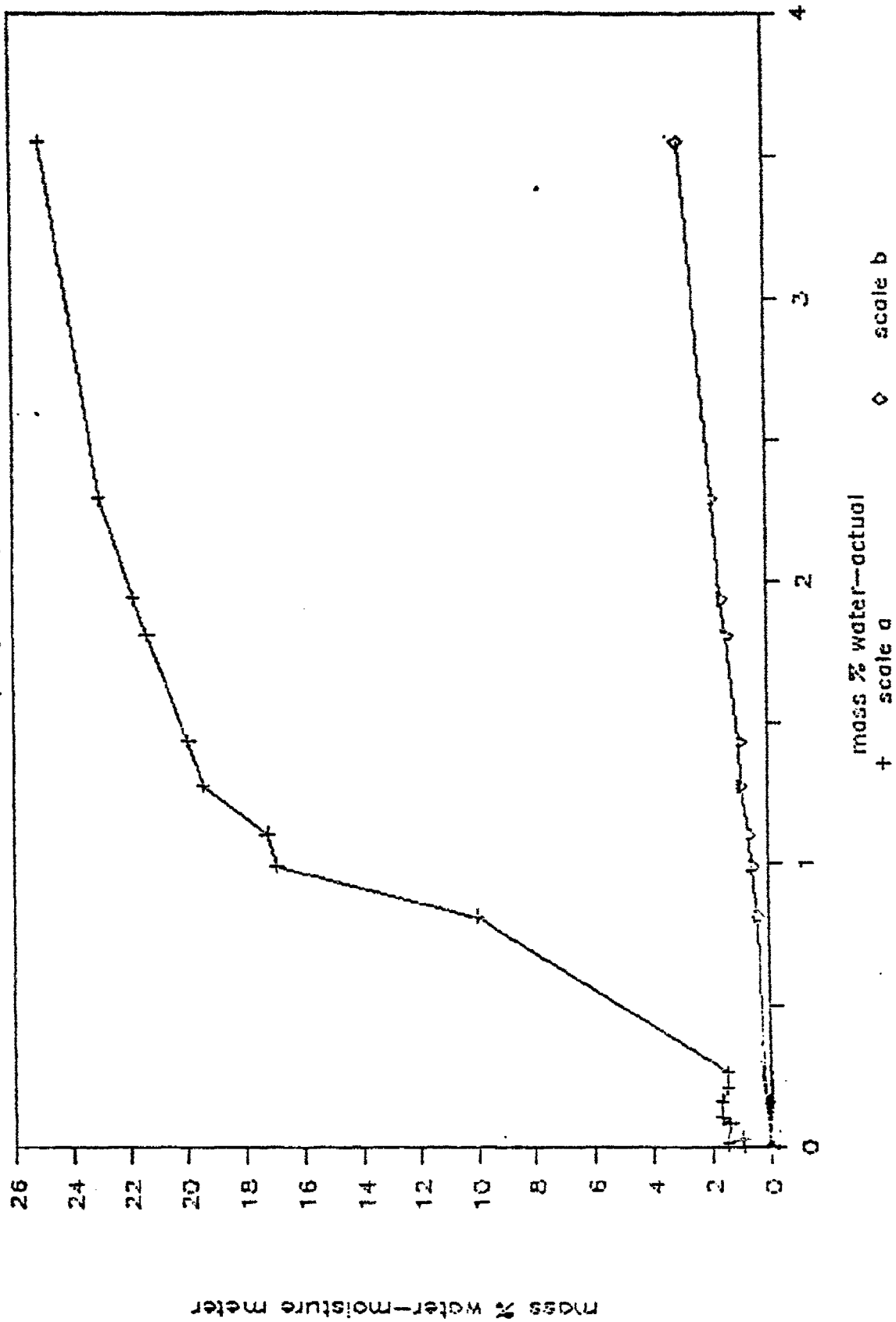


Figure 33. —moisture meter calibration
(with gel coat)

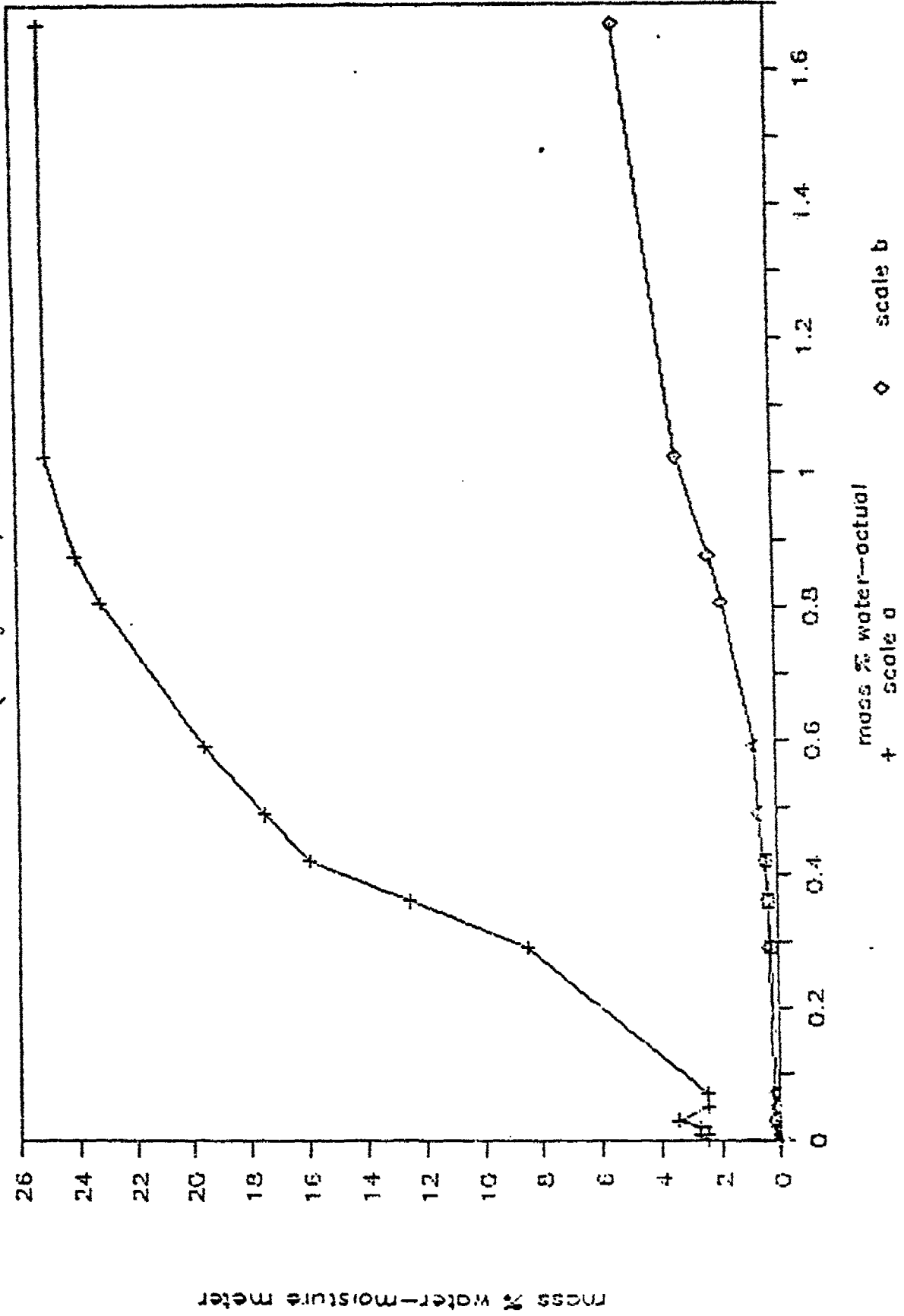


Figure 34. - moisture meter calibration
 (no gel coat)

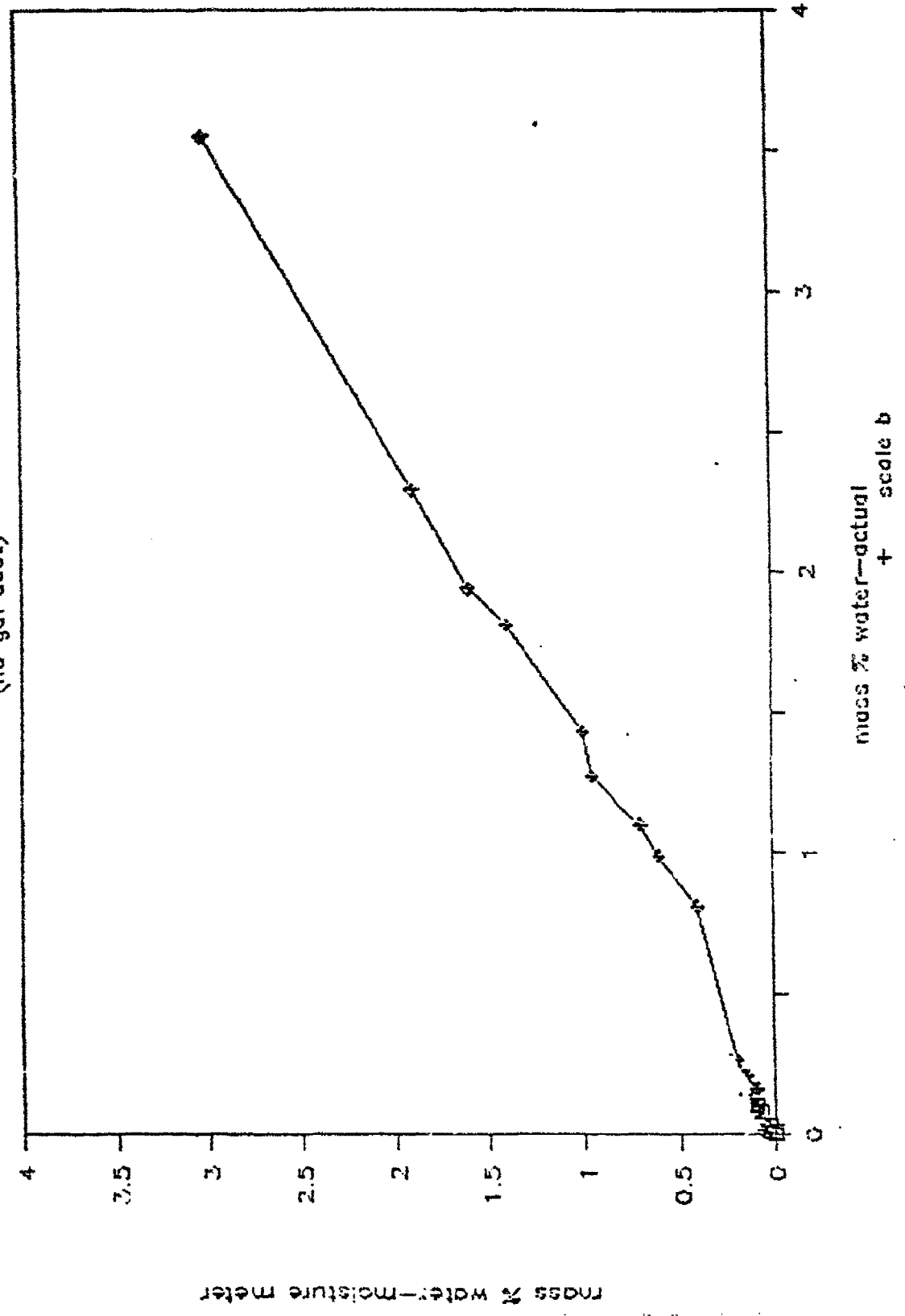
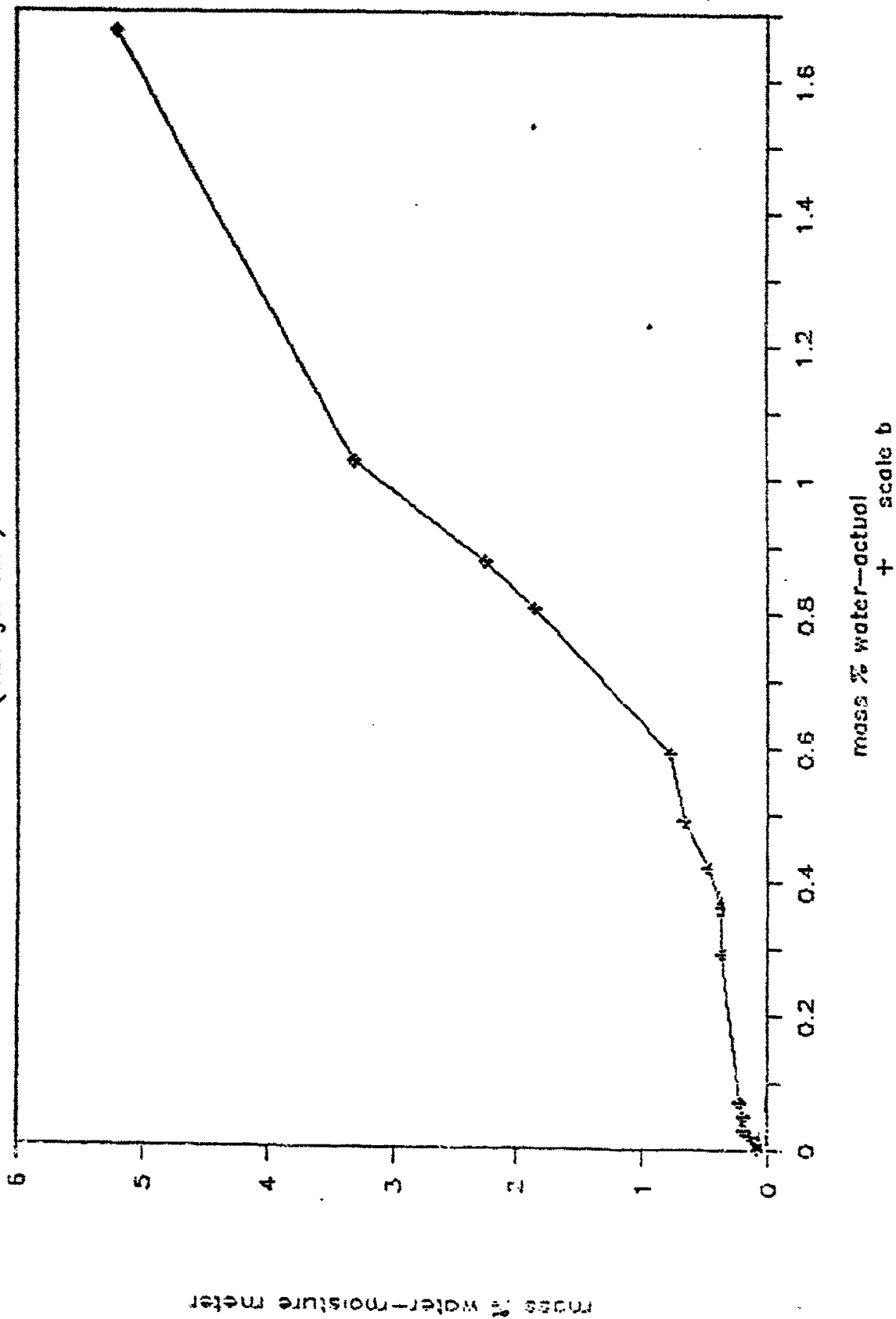


Figure 35. —moisture meter calibration
(with gel coat)



One of the most significant observations from the data shows that the scale readings have limitations. The relationship between the reading and moisture content is non-linear. The meter readings never reach zero percent even when the composites are totally dry. Another important factor is that the readings are relative rather than absolute and the readings also depend on the amount of contact between the meter and the hull. Measurements should be considered over various points in a specified area and taken as averages for better accuracy. The two fully saturated hull materials prepared by us have water contents of 1.5 to 3.5 percent. Field readings, using moisture meters, have been reported as much as 20 percent and more. These values are misleading and probably are taken on the manufacturer's recommended scale A. Several boats examined by us after winter drying showed moisture contents of 0.15 to 0.2 percent using scale B. Readings taken near the rudder and engine were affected by the underlying metal and gave spurious results. Scale B readings varied from 0.3 to 0.6 percent while A-scale readings, in the same area, ranged from 3 to 17 percent. Readings on a boat, which had never been in the water, were 0.2% on the B scale and 2 to 10% on the A scale.

Given the limitations, the drying process, at least at shallow depths, can be followed using commercial moisture meters. The reading the moisture meter are not true moisture content. When the readings reach a constant value, only the surface is approaching dryness. The interior, which must be dried below the saturation level, could still be water laden. Therefore, while the meters are useful, they should not be relied upon to determine the duration of the drying process.

12.2 Recommended Drying Procedures:

The safest method for determining the drying time of a hull is to take a plug sample from the hull. Cut a 1 mm slice (transverse to the gel coat) from the sample and dry it at 100°F until a constant weight value is obtained. This should take about 20 hours. To find the weight percent of water in the laminate, use the following relationship:

Starting wt. - Dry wt.

starting wt. X 100 = wt. percent water

It is important that the core sample be sectioned as soon as it is cut. The 1 mm slice should be weighed and dried as soon as it is sectioned, otherwise erroneous results will be obtained.

The edges of the core sample must be coated with 2 or 3 layers of an epoxy to cut down edge losses. This sample should be held at the same conditions as those to be used for hull drying. The hull sample should be weighed each day until no more than 0.5 percent water remains in the hull sample. While a totally dry hull would be ideal, the drying time would be so long that it would be impractical. A safe level for repair is a maximum of 0.5 percent water.

To find this target weight follow this procedure:

1. Weigh the plug sample (W_p). A 2" plug should weigh about 30 grams. $W_p = 30$ gms.
2. Coat the edges with epoxy (e) and reweigh to get the weight of the epoxy + plug. ($W_p + e = 30.3$ gms).
3. Subtract to get the epoxy weight. $(W_p + e) - W_p = W_e$
($W_e = 0.3$ gms).
4. Multiply the plug weight by the percent of water (%w) found from the slice drying experiment to find the weight of water in the plug sample (W_w). The percent of water should range from 0.6 percent to 6 percent depending upon the condition of the hull. $(\%w \cdot W_p = W_w$. As an example, a 30 gram plug, with 3 percent water will yield 0.9 grams of water. $(.03) (30) = 0.9$ grams water.
5. Subtract this water weight, w_w , from the weight of the plug (W_p) to get the weight of the dry hull material (W_D).

$$(W_p - W_w) = W_D \text{ or } 30g - 0.9g = 29.1 \text{ gms.}$$

6. Take 0.5 percent of this weight to find the amount of water which is permissible to be left in the hull (W_{SXW}).

$$W_{SXW} = (W_D) \cdot (0.5\%) (29.1) (.005) = .1455g.$$

7. Add this weight (W_{SXW}) to the dry weight (W_D) and to the weight of the epoxy to get the target drying weight for the core sample.

$$\text{Target weight} = W_{SX} + W_D + W_e$$

$$\text{Target weight} = (0.1455g) + (29.1g) + (0.3g) = 29.5455g$$

The epoxy edge-coated core sample, weighing 30.3 grams must be held under the hull drying conditions until it weighs 29.5455 grams.

This is a two sided drying condition. The plug is losing water from both the gel coat side and the bilge side. The hull drying conditions must duplicate this. The bilge must be exposed to circulating and dehumidifying conditions.

12.3 Recommended Drying times:

For those repairers who do not wish to core the hull or for those who do not have the analytical balances necessary to conduct the weighing experiments, the following drying times are recommended based on our experimental drying results. These recommendations are for fiberglass-polyester hulls that do not contain wood or foam layers inside the hull. The hull section must not be more than 1/2" thick. They are also for two sided drying conditions, i.e. good circulation of dry air inside the bilge.

Dry the hull for 16 days at 100°F if the relative humidity of the air is approximately 50 percent; or for 32 days at 83°F, or for 64 days at 65°F, or for 128 days at 47°F. The following times can be used if the relative humidity is kept at 25 percent. Nine days of drying are needed at 100°F, 18 days at 83°F, 36 days at 65°F and 72 days at 47°F.

The above are average figures expected to serve as a guideline for fiber glass hulls with orthophthalic and isophthalic acid based resin matrix materials. The drying must be continuous at these conditions and should not be started until thorough washing and rinsing of the prepared surface has been completed.

13. Types of Coatings Investigated

A coating is a material applied over a substrate material to serve aesthetic and/or protective purposes. Typically, a coating applied to a boat hull must serve both these purposes.

To have aesthetic value, the coating must be (1) colorable in a wide range of colors, (2) have high gloss, (3) be durable under the conditions used, and (4) be weather and UV resistant. In most cases, the coating must also be easily applied and economical (6).

Of greatest importance to marine applications, the coating must protect the fiberglass reinforced polyester substrate. To protect the substrate the coating must have the following characteristics:

1. Toughness. The coating should "absorb" some of the stresses imparted to the laminate, therefore protecting the substrate from physical damage.
2. Durability. It should maintain all its characteristics under the conditions of use for a reasonable amount of time. This includes color, gloss, surface appearance, physical, chemical or mechanical properties. It must not undergo physical or chemical breakdown such as cracking, peeling or blistering.
3. Compatible Mechanical Properties. The coating must have adequate strength and be compatible with the substrate. Matching of the modular of elasticity (E) of the coating and the substrate will minimize the stresses

at the interface. For example, if the coating has a higher modulus of elasticity (E) than the substrate, then, under a given load, the substrate will deform more than the coating (see Fig. 36). This will result in a differential stress at the interface of magnitude

$$\frac{\Delta E}{E_1 E_2}$$

If the bond between the coating and substrate is poor, this may lead to peeling of the coating or coating blisters. However, if the bond is good, this will lead to the generation of tensile stresses in the coating which may be relieved by cracking of the coating.

If the modulus of the coating is less than that of the substrate (Case 2) then the reverse situation will result. The magnitude of the stress at the coating/substrate interface will still be $\Delta E/E_1 E_2$. In this case the coating will deform more than the substrate under a given load. Again, if the bond between the two is poor, this may result in the coating debonding from the substrate. However, if the bond is strong, it will generate tensile stresses in the substrate, below the interface. This could result in crack formation, in the substrate.

4. Swelling and Thermal Expansion. Compatibility of these parameters with the substrate is important to minimize stresses produced at the coating/substrate interface. Just as a load can change the dimensions of a material, heating or swelling can also change the volume of a material. Therefore, the thermal coefficient and the swelling coefficient must also be compatible.

The analogy can be made to two different materials of different thermal coefficients of expansion α (see Figure 37). At a given temperature, if the coating has a lower thermal coefficient of expansion than the substrate, this would be analogous to Case 1. However, if the substrate has a lower thermal coefficient of expansion than the coating, the

stresses produced can be described by Case 2.

Differential swelling between the coating and substrate also leads to interfacial stresses. Every polymer, depending on its composition and molecular structure, absorbs different amounts of water at different rates. Each polymer responds differently to different amounts of water by swelling. This is shown in Figure 38. The slope of these lines can be described as the "modulus of swelling" or "coefficient of swelling".

The stress produced, at the interface, between two different materials, of different "moduli of swelling", cannot be described as simply as in the other cases. Another parameter must be introduced. This is water concentration.

Exposed under identical conditions, different polymers will absorb different amounts of water. If two polymers are put together, as a coating over polyester resin, at equilibrium or non-equilibrium conditions, there will be a step jump in the concentration of water at the interface.

The way stresses can be produced at the interface can be summarized by the three following situations using Figure 38.

Case I--The coating and the substrate, at the interface, have the same concentrations of water (highly unlikely). The differential swelling would be ΔI and the stress, as a result, would be proportional to ΔI .

Case II--The substrate contains less water than the coating at the interface. The differential swelling at the interface would be ΔII , which is also proportional to the stress. This situation would lead to a larger stress produced at the interface than in Case I.

Case III--The substrate contains more water than the coating at the interface. This leads to a lower stress produced at the interface than in

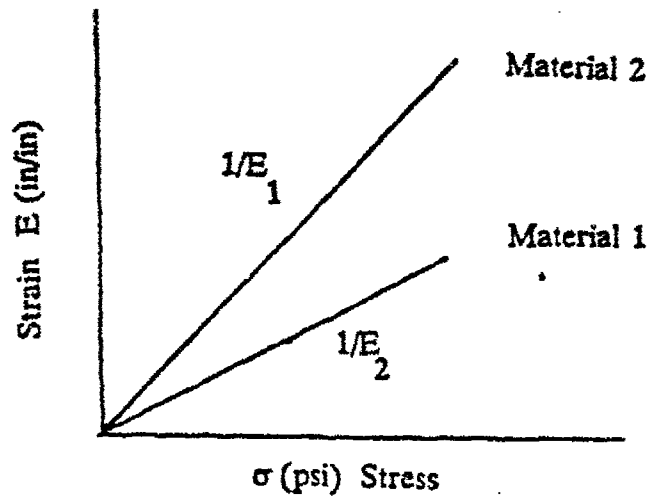


Figure 36. Strain vs. Stress

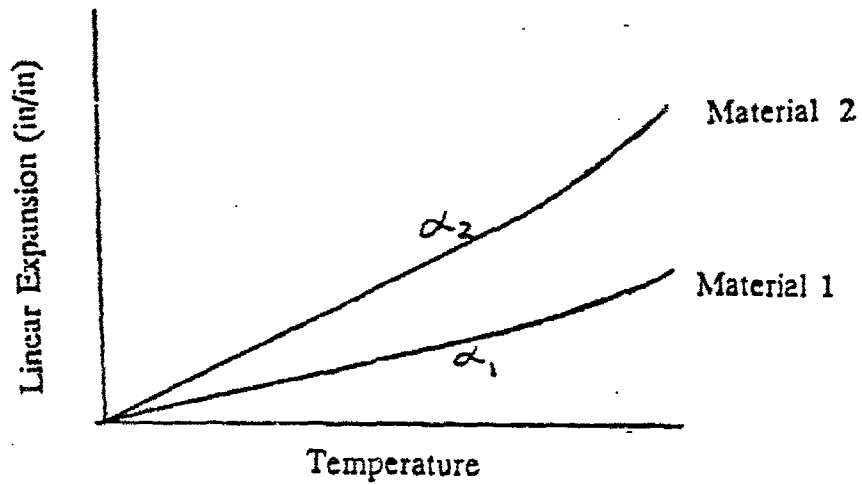


Figure 37. Linear Expansion vs. Temperature

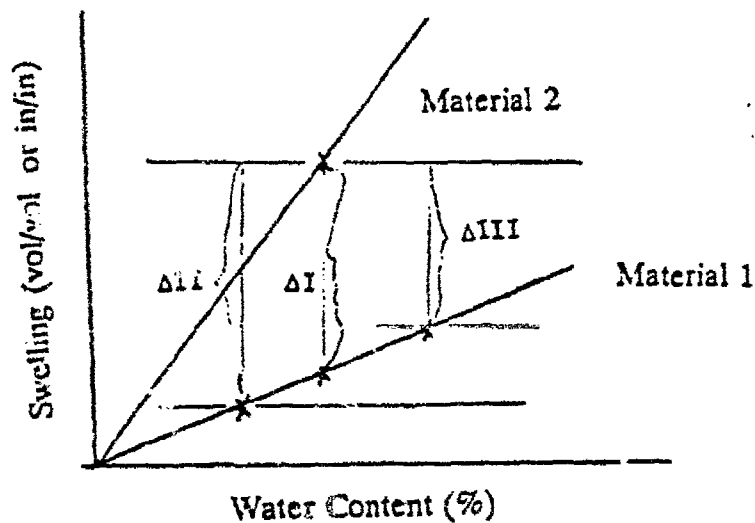


Figure 38. Percent Swelling vs. Percent Water Content

Case I.

Case III is most favorable, from this it can be seen that if two materials are chosen very carefully, stresses due to differential swelling, can be minimized significantly or eliminated completely.

If the coating swells less than the substrate then the stresses produced at the interface can be described by Case 1. However, if it swells more than the substrate then it would be analogous to Case 2.

This type of swelling appears to be very important in blistering. As the coating tries to swell it is constrained by the interfacial bond. It creates a surface waviness. Under the crests, a tensile field, normal to the surface, can aid in initiating disk cracks and blisters just below the interface.

5. Hydrolytic Stability The coating must be stable in water in order for it to be able to act as a barrier coat against water permeation into the underlying laminate. Hydrolytic stability is largely governed by the number of hydroxyl groups and ester linkages, in the polymeric matrix, that would be susceptible to attack by water (7). Coatings that are hydrolytically more stable are less prone to degradation and hence will serve more effectively in protecting the substrate. Water soluble materials, undercure, stresses, and fillers play an important role as well in water permeation and hydrolytic stability.

6. Low Shrinkage on Curing. Shrinkage must be low in order to minimize shrinkage stresses at the coating/substrate interface. Once a coating is applied over the reinforced polyester resin substrate, some chemical bonding begins to take place between the two. This sets the coating essentially into place at this point. As the coating continues to cure or dry it wants to shrink but it is partially constrained by the chemical bond with the polyester resin. This constraint imposes a tensile stress, in the coating, above the interface. Shrinkage stresses may lead to

microcrack formation in the coating.

All the properties discussed are important in selecting a coating. The major interests of the study are the protective properties of the coating against water permeation and blistering.

It must be noted that thermal and water concentration gradients almost always exist through a laminate. This is particularly true for a boat hull. The inside of the hull is exposed to the bilge and sees different temperature and humidity conditions than the outside of hull which is exposed to water and the atmosphere. These gradients alone in a material can cause microcracking or aid diffusion.

13.1 Components of a Coating

Coatings may be clear single phase materials or comprised of a continuous phase and a discontinuous phase. All paints are two phase materials. The continuous phase is comprised of a polymer or a binder that forms a continuous film on curing by reacting with itself or by releasing a solvent or a diluent. The film forming polymer is what protects the substrate (6).

The solvent or diluent provide the means by which the coating is applied (6). In some cases the solvent can be incorporated into the polymer film as in the case of styrene in polyester resin.

The discontinuous phase includes additives such as flowing agents, catalysts etc.; primary pigments which are fine particulate organic or inorganic compounds (they give opacity, color and anticorrosive properties to the coating) and extenders which are coarse inorganic compounds that give the coating opacity, sanding properties and they lower the cost of the coatings significantly (6).

13.2 Curing of Coatings

Curing of a paint or a solvent based coating takes place through evaporation of the solvent. On drying, the film converts from a low molecular weight polymer to a highly crosslinked three dimensional network.

Cure of solventless coatings--such as epoxies, polyester resin, two-part polyurethanes, etc., takes place through the reaction of constituents in the film and is begun by the addition of a catalyst or a curing agent (6).

Solvent based coatings have the disadvantage that their early life properties are determined by the presence of the solvent. These properties include hardness, flexibility and water permeation (6). These properties change as the last portion of solvent is lost. The volume change, on setting, of these coatings, is much greater than solventless coatings.

13.3 Coating Types

Six different types of coatings have been selected for evaluation of their resistance to water permeation, blistering, and hydrolysis. They are the following:

1. polyester gel coat
2. epoxies
3. polyurethane
4. phenolic resin spar varnish
5. alkyd enamel based bottom paints
6. antifouling paint.

A brief description of their properties and chemistry will be given below.

1. Polyester Gel Coats

If an organic acid is reacted with an organic base an ester is formed. If the reaction produces a chain molecule with many units joined at ester linkages, the material is known as a polyester. A great degree of freedom is

possible in forming polyesters chains. Many acids (orthophthalic, isophthalic, maleic, fumaric, etc.) and glycols (OH containing organic bases), with various hydrolytic properties, can also be used. If the polyester is to be used for making a gel coat or resin, the number of carbon double bonds, i.e. the degree of unsaturation, can be varied. This controls many of the resin's properties. These double bonds react with the styrene or other monomers to crosslink the polyester liquid into a solid boat building material. The reaction is begun by addition of catalyst to the resin.

If isophthalic acid is used rather than orthophthalic acid, the ester linkage is less susceptible to water attack but it allows water to diffuse more rapidly. In making the resins, the degree of unreacted material and the amount of impurities can have an important effect on the hydrolytic stability of the resin. This can outweigh the effects of various chemicals used in building the polyester chains.

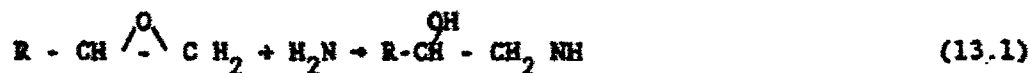
A typical gel coat material has a thixotrope added, usually colloidal silica, to prevent run-off of the material once it is sprayed onto the mold surface. Extenders are added to some materials and these can effect water absorption properties. To color the gel coat various pigments are added. The finished product is then catalyzed and sprayed or rolled onto the surface to form the outer surface of the boat hull.

2. Epoxies

In the marine industry today, epoxy based coating materials are widely used and suggested for the repair of a blistered boat. Increased usage of epoxies stems from their excellent properties. These include outstanding mechanical properties, toughness, rigidity, excellent chemical resistance, particularly to alkalies (8), thermal and hydrolytic stability, relatively low permeability to water, low shrinkage on curing (9) and good adhesion to a wide variety of substrates (10).

Epoxies are characterized by their epoxide groups $R-CH \begin{matrix} \diagup O \\ \diagdown \end{matrix} CH_2$ (9).

Cure of epoxy resins usually takes place with the addition of an amine based curing adduct, which is typically six weight percent of the epoxy resin (8). Cure of the epoxy resin takes place through reaction of amine groups with terminal epoxide groups. The reaction is described as follows:



The reaction between the two does not release any volatiles or water (9).

A wide variety of epoxy resins and curing agents are available and therefore, following cure, epoxies with a broad range of properties can be formulated. Epoxide groups, which are chemically very inert, impart the polymer with good chemical resistance. Aromatic groups in epoxy resin also increase chemical resistance (9). Toughness comes from the wide spacing between epoxide and hydroxyl groups and by lowering the degree of crosslinking in the cured polymer (9). Rigidity comes from aromatic groups crosslinking (11). By replacing aromatic groups with aliphatic or cycloaliphatic groups the flexibility of the cured polymer increases (10,11). Aromatic rings and amide linkages give good thermal stability. Good adhesion comes from the polar hydroxyl groups that always remain. Finally, shrinkage during cure can be reduced by lowering the crosslinking density (11).

One disadvantage of epoxies is that during curing, in high humidity conditions, a chemical blush forms on the surface (12). This is a sticky tacky layer that can be removed easily. Impurities such as water, organic solvent and inorganic salt alter the curing and physical properties of epoxies. Another disadvantage of epoxies is that they are difficult to work with. Amines are skin irritants. They must be handled with care and used with adequate ventilation.

There are two types of epoxy based coatings, solvent and solventless. Solventless epoxies are characterized by short pot life, 25 - 30 min, and high viscosity (9). Usually a nonreactive diluent is used, such as pine oil, dibutyl phthalate, xylene or a reactive diluent such as butyl glycidyl ether. (8). To lengthen the pot life of these epoxies, a ketamine curing agent is

sometimes used. Ketamines are formed by the reaction between a polyamine and a ketone solvent (8).

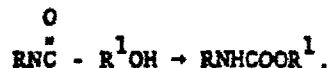
In solvent based coatings, cure takes place through evaporation of the solvent. Typical solvents used are xylene, sec-butanol or a mixture of the two. (8).

Other additives can be incorporated into epoxies such as coal tar pitch (8). Coal tar epoxies are claimed to have excellent chemical resistance low permeability to water, good adhesion and high flexibility (8). Coal tar epoxies usually contain a lower molecular weight epoxy resin (8). Cure takes place by addition of an amine curing agent. Many times, the coal tar pitch is incorporated into the curing agent because, even though coal tar pitch is considered unreactive, it may contain phenolic hydroxyl groups that can react with epoxide groups (8). Coal tar epoxies usually contain 60 to 65 percent coal tar pitch (8). Higher contents of coal tar lead to coatings of poorer chemical resistance (8).

2. Polyurethane

Polyurethane based coatings are accepted for their good chemical, solvent and abrasion resistance, excellent toughness and flexibility and good heat and hydrolytic stability (13,14,15).

Polyurethanes are identified by the urethane bond, $\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$. Polyurethane based coatings may contain other functional groups such as esters, ethers, ureas, amides, epoxies etc.. Polyurethane is formed by reaction of an polyisocyanate with a hydroxyl containing compound. The reaction is described as follows:



Commercially available polyurethanes contain about 10 percent di- or

polyisocyanates and di - or polyhydroxyl compounds (17).

R and R¹ groups can be chosen to tailor films with variable properties. R² groups based on terephthalic and phthalic acid give harder coatings (18). Aromatic polyurethanes have tendencies of yellowing in sunlight, while those made with aliphatic polyisocyanates do not. They also have better resistance to hydrolysis and heat degradation (19).

Polyurethanes are classified into six basic categories according to the curing mechanism (20). Four of the six classes are one part polyurethanes. The core of type one polyurethanes is based on drying oils. Type two is based on a moisture cure. Type three cure only takes place at elevated temperatures and type six curing is based on preheated urethane polymers. For types four and five cure takes place through the addition of a curing agent. For a type four polyurethane, the base is an isocyanate terminated polymer and the curing agent is a di or polyfunctional hydroxyl containing compound. For a type five polyurethane, the base is a hydroxyl terminated polymer and the curing agent is a di or polyfunctional isocyanate containing compound. Type five polyurethanes are most commonly used for marine applications because they have the best moisture barrier properties. (R).

Like epoxies, polyurethanes are also skin irritants and must be handled with care and used with adequate ventilation.

4. Phenolic Resin Spar Varnish

Phenolic resin based spar varnishes are claimed to have very high resistance to water and alkalies. On curing they form very hard glossy films (21). One disadvantage of these coatings is that they yellow with exposure to sunlight (22). Incorporation of other resins can lead to more flexible coatings that are less susceptible to discoloration (23).

Phenolic resins are produced by reacting phenol with formaldehyde in combination with other resins (24). A drying oil is used to dilute the resin

so it can be applied and cured. Modified wood or linseed oils give high resistance to water and are used in varnishes. For marine application, the resin is modified rosin oil and the diluent is aromatic or white spirits (24).

There are two basic types of phenolic resins, novalacs and resoles. Novalacs are thermoplastics. For novalacs, the phenol used is substituted on the para position by alkyl groups. Resoles, on the other hand, are thermosetting. The phenol is substituted in both the ortho and para positions and therefore resoles are more crosslinked than novalacs. Resoles are used in varnish paint formulations. (26).

5. Alkyd Enamels

Alkyd resins or enamels are formed from polyesters derived from vegetable oil triglycerides or polyols such as glycerol and dibasic acids or their anhydrides, such as phthalic anhydride or orthophthalic acid (27). An oil or oil derived fatty acid is chemically combined into the polyester structure (28). The oil length is characterized as short, medium or long, depending on the molecular weight (29). Long and medium length oils are used in the marine industry because they give more durable, tougher and better moisture resistant films (30). Aromatic acids such as phthalic or maleic anhydride make the coatings more flexible. Isophthalic acids give more harder and durable films and better drying characteristics (34).

Cure of alkyd enamels takes place through evaporation of the solvent phase which is typically white spirits or some other aromatic solvent (32).

Disadvantages to alkyd enamels are that they absorb appreciable amounts of water. This results in significant swelling of the coating which may lead to coating blisters (33). An important new class of alkyd enamels are blends which contain some amount of urethane and/or silicone to give improved properties.

6. Antifouling Paint

Antifouling paints are applied to the bottom of a boat hull to prevent attachment of marine organisms and plants such as seaweed. Fouling on a hull significantly increases drag on the boat and hence fuel consumption. In some cases, fuel consumption may be increased as much as 30 percent (34).

Antifouling paints are comprised of a soluble phase and an insoluble matrix. The insoluble constituent may be an, epoxy, vinyl, alkyd or phenolic resin. The soluble component is what prevents fouling. Popular antifoulants are cuprous oxide, which may be as much as 75 percent of the paint, and tributyl tin (35).

The antifoulant dissolves away at a particular rate which is usually logarithmic. A typical rate for cuprous oxide is 10 mg of Cu/Cm²·day (36). Because part of the coating dissolves away it must be reapplied periodically.

Recent findings suggest that tributyl tin (T.B.T.) may be a dangerous pollutant which is incorporated in the food chain by shell-fish. As a result it has been banned in certain areas.

While there are many other types of coatings, our experiments were limited to these materials since they are commercially available for use in the marine industry.

14. Performance of Repair Coatings

The performance of various coatings as potential repair materials for boat hulls were evaluated for three different situations:

1. Coatings were applied over the gel coat of a new laminate. The objective of this is to see if a coating on a new boat hull will delay or prevent the onset of blisters. The test also served to evaluate the effectiveness of a

coating material as compared to an equal thickness of gel coat. (Sample series 201)

2. Coatings were used in place of a gel coat. They were applied over a new laminate as a substitute for a gel coat. This is to determine the performance of a coating in place of a gel coat. (Sample series 202)
3. Coatings were applied over blistered samples after removal of the gel coat and various repair procedures. This is to determine the performance of the coatings as repair materials. (Sample series 200)

For all tests, the samples used were from the very large panel with an orthophthalic acid based gel coat and laminating resin discussed in Section nine. Some of the samples used in the experiment, discussed in section nine, were used to evaluate the coatings as repair materials.

One other set of samples was used to help evaluate repair materials and techniques. These samples came from a severely blistered boat donated to us by a boat manufacturer. The boat hull was cut into 4" x 4" test samples. (Sample series 203)

14.1 Coating Procedures

Eleven different coatings were evaluated. All are commercially available and are recommended for use in a marine environment. These are:

- alkyd enamel based bottom paint
- urethane-silicone-alkyd blend based bottom paint
- silicone-alkyd enamel based bottom paint
- phenolic resin based spar varnish
- cuprous oxide-epoxy based antifouling paint
- two-part polyurethane blend
- urethane-epoxy blend
- two-part, system - penetrating epoxy and overcoat filled epoxy
- high solids content epoxy
- penetrating epoxy
- coal tar pitch based epoxy

Table 5 summarizes the coating number designation, type of coating, method of application, total number of coats, preparation between coats, cure time between coats and minimum cure time before water immersion. All manufacturers procedures were followed for all samples sets, except for the 202 series of samples, where double the recommended number of coats were used. For sample series 200, 201 and 202, each sample will be labelled using the coating number designation and a letter a - d which designates samples within a particular coating set. Coating number 12 means gel coat only, no coating.

14.2 Series 201 - Coating Over a Gel Coat of a New Laminate

Forty-six samples, chosen randomly among over 200 ortho/ortho samples, produced by a local boat manufacturer, were used for the study. Four samples were tested per coating type.

Prior to coating, the gel coat was scrubbed with soap and water to remove sawing debris followed by a manufacturers' recommended pre-coating solvent wash in order to remove waxes and oils, sanded with 80 grit sandpaper and again scrubbed with soap and water and washed with the solvent. The samples were dried thoroughly before coating.

The total wet coating thicknesses were targeted to 10 mils. A mil gauge was used. Procedures listed in Table 5 were followed for each coating.

All samples were monitored for blister initiation time, blister severity, coating blisters, deterioration, as well as for any other notable change. Two samples from each coating set were immersed in distilled water at 65 °C. The other two from each set were exposed to 65°C water, on the coating side only, for a period time and then totally immersed in water at 65°C. These samples were weighed periodically to analyze differences in weight gain of the samples among the different coatings.

Upon completion of experimentation, coating and gel coat thicknesses were measured from a section of each of the samples. Blisters were punctuated

Table 5. Coating Description and Application Procedure

Coating Number Designation	Coating Type	No. of Parts	Ratio (vol) Base: Accelerator	Method of Application	Total Number of Coats	Preparation Between Coats	Drying Time Between Coats (hrs.)	Minimum Cure Time before immersion (days)
1	Alkyd Enamel	1	1:0	brush	2	sand/rinse/dry	OH	14
2	Silicone Alkyd Enamel	1	1:0	"	2	" " "	OH	14
3	Phenolic Spar Varnish	1	1:0	"	2	" " "	OH	14
4	Alkyd Enamel Blend	1	1:0	"	2	" " "	OH	14
5	Polyurethane	2	3:1	"	2	" " "	OH	14
6	Top Coat Epoxy	2	5:2	"	4-5	" " "	2-18 (ws)	14
	Penetrating Epoxy (undercoat)	2	3:1	"	2	" " "	4-24 (ws)	
7	Urethane-Epoxy Blend	2	3:1	"	2	" " "	2-8 (ws)	7-10
8	High Solids Epoxy	2	5:1	"	2-3	" " "	OH	3-4
9	Coal Tar Epoxy	2	9:1	"	2-4	" " "	2-4 (ws)	7-10
10	Cuprous Oxide Anti-fouling Paint	1	1:0	"	2	" " "	OH	14
11	Penetrating Epoxy	2	5:1*	"	3	" " "	OH	7-10
12	Coat	2	1:02*	spray	1 (20-25 mils)	" "	" "	14 (min-5mm)

Key: sand- light sanding with 80-250 grit sand paper
 rinse- light rinse with water to remove sanding debris
 OH- overnight drying (18-24hrs.)
 ws- recommended re-coating time without sanding
 * - ratio by weight

randomly to measure blister fluid pH using pH paper. For a selected set of samples, thin cross-sections were made using a diamond saw, later to be used for microscopic observations.

14.3 Results from Series 201

Results for series 201 are summarized in Table 6. The table presents gel coat and coating thickness, blister initiation time, blister density and severity (taken at monthly intervals), total immersion time in water at 65°C and blister fluid pH. Those samples that were exposed to one sided immersion for a period of time are designated with a star next to the sample number.

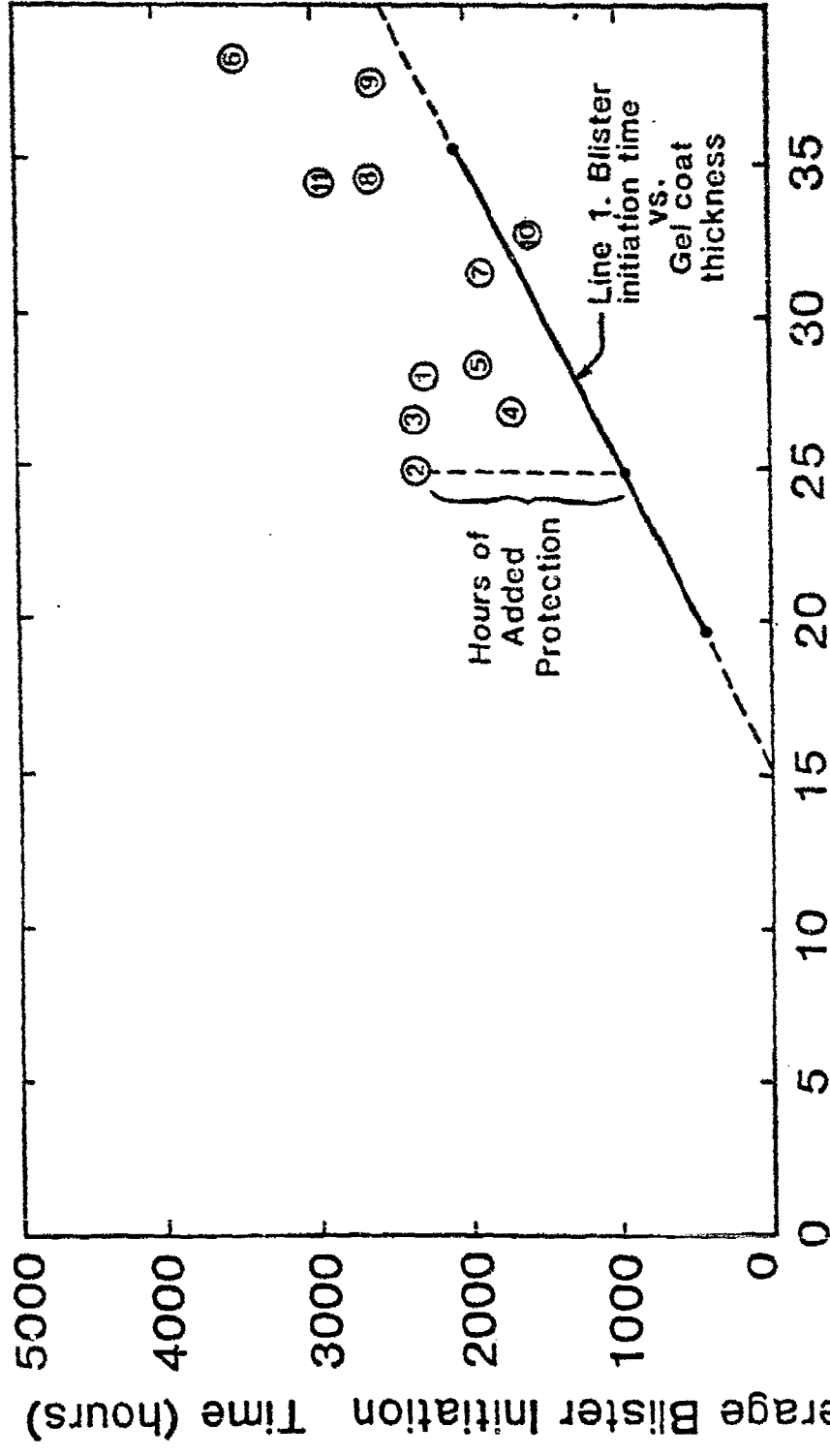
All sample designated with the letter "d" from each coating set, and sample 12 b, had blister initiation times that fell far below any of the others in the set. These samples were exposed to water on one side for a period of time but were weighted very frequently. Repeated heating and cooling, repeated drying and wetting and repeated bending may produce surface microcracks. This will speed up the blister initiation time. For this reason these samples will not be used to evaluate the coatings.

In order to determine which coating delays the onset of blistering best, the data must be normalized to gel coat and coating thicknesses. Generally, the thicker the total coating the greater the blister initiation time. Without normalizing to thickness a sensible comparison cannot be made among the coatings. Although the wet coating thickness was targeted to 10 mils, on curing, each coating shrunk by a different amount. Also, variations in gel coat thicknesses for these samples, as discussed in Section 9 played a major role on blister initiation times.

Fig. 39 shows, for samples a-c of each coating, the average blister initiation time vs the average combined gel coat and coating thicknesses (Line one). It can be seen that there is a general trend of increasing blister initiation time with increased total coating thickness. Line two represents blister initiation time vs gel coat thickness for samples taken from the large

Table 6. Results for Series 201 - Coating Over a Gel Coat, at 65°C

Sample #	Coating thickness (mils)	Gel coat thickness (mils)	Blister Initiation time (hrs)	1 Month		2 Months		3 Months		4 Months		5 Months		Total Immersion time (hrs)	Blister Fluid
				Blister Density (blister/cm ²)	Max Blister Size (cm)	Blister Density (blister/cm ²)	Max Blister Size (cm)	Blister Density (blister/cm ²)	Max Blister Size (cm)	Blister Density (blister/cm ²)	Max Blister Size (cm)	Blister Density (blister/cm ²)	Max Blister Size (cm)		
201-1A *	2.4	27.6	2247±24	None	-	None	-	None	-	2 blisters	5.5	2 blisters	10.5	4106	3-3.5 Acidic odor
201-1B *	2.2	23.6	2713±95	None	-	None	-	None	-	2 blisters	-	2 blisters	3.5	4106	3-3.5 Acidic odor
201-1C *	2.4	25.6	1911±84	None	-	None	-	3 blisters	-	1 blister	5.1	1 blister	9.0	4106	3-3.5 Acidic odor
201-1D *	1.8	25.6	622±96	0.24	0.24	0.16	-	1 lg. blister	-	1 lg. blister	4.4	1 lg. blister	10.85	4106	3-3.5 Acidic odor
201-2A *	2.1	23.6	2079±84	None	-	None	-	None	-	3 blisters	3.45	3 blisters	5.0	4106	3-3.5 Acidic odor
201-2B *	2.6	15.8	2390±59	None	-	None	-	None	-	1 blister	-	1 blister	2.9	4106	3-3.5 Acidic odor
201-2C *	2.6	27.6	2533.5±84.5	None	-	.32	-	None	-	-	-	-	-	1342	3-3.5 Acidic odor
201-2D *	2.0	27.6	814±96	None	-	None	-	None	-	1 lg. blister	5.3	1 lg. blister	12.3	4106	3-3.5 Acidic odor
201-3A *	2.6	25.6	2247±84	None	-	None	-	None	-	1 blister	2.25	1 blister	2.9	4106	3-3.5 Acidic odor
201-3B *	2.7	23.6	2390±59	None	-	None	-	None	-	few blisters	-	few blisters	0.48	4106	3-3.5 Acidic odor
201-3C *	3.9	19.7	2390±59	None	-	None	-	None	-	-	-	-	-	1342	3-3.5 Acidic odor
201-3D *	3.5	21.6	443±83	0.8	1.43	1.20	-	Many blisters	-	0.64	4.4	0.64	6.75	1342	3-3.5 Acidic odor
201-4A *	2.2	19.7	815.5±48.5	None	-	None	-	None	-	2 lg. blisters	7.0	2 lg. blisters	12.2	4106	3-3.5 Acidic odor
201-4B *	2.0	25.6	2247±84	None	-	None	-	None	-	0.64	0.9	0.64	6.3	4106	3-3.5 Acidic odor
201-4C *	2.95	27.6	2247±84	None	-	None	-	None	-	-	-	-	-	1342	3-3.5 Acidic odor
201-4D *	2.95	15.8	443±83	0.4	1.0	0.56	-	2 blisters	-	1 lg. blister	-	1 lg. blister	9.0	4106	3-3.5 Acidic odor
201-5A *	2.75	27.6	1717±110	None	-	None	-	None	-	0.56	.12	0.56	8.3	4106	3-3.5 Acidic odor
201-5B *	3.5	23.6	2247±84	None	-	None	-	None	-	0.72	.18	0.72	.32	4106	3-3.5 Acidic odor
201-5C *	3.5	23.6	1911±84	None	-	None	-	1 blister	-	-	-	-	-	1300	3-3.5 Acidic odor
201-5D *	3.5	25.6	478±48	1.04	.09	None	-	None	-	1 lg. blister	-	1 lg. blister	7.5	4106	3-3.5 Acidic odor
201-6A *	None	35.4	2533.5±84.5	None	-	None	-	None	-	-	-	-	-	4106	3-3.5 Acidic odor
201-6B	Bottomcoat 7.8	25.6	4022±84	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-6C	Topcoat 5.1	19.7	4022±84	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-6D *	Topcoat 5.5	27.6	622±96	0.8	.12	None	-	None	-	-	-	-	-	1200	3-3.5 Acidic odor
201-7A *	5.6	25.6	1911±84	None	-	None	-	1 sm. blister	-	1 lg. blister	-	1 lg. blister	7.8	4106	3-3.5 Acidic odor
201-7B *	2.75	29.5	1283.5±156.5	None	-	None	-	2 lg. blisters	-	2 lg. blisters	6.5	2 lg. blisters	9.5	4106	3-3.5 Acidic odor
201-7C *	3.2	27.6	2533.5±84.5	None	-	None	-	None	-	3 blisters	1.3	3 blisters	8.4	4106	3-3.5 Acidic odor
201-7D *	2.6	23.6	478±48	.56	3.15	None	-	None	-	1 lg. blister	-	1 lg. blister	2.8	1300	3-3.5 Acidic odor
201-8A *	13.0	15.7	1283.5±156.5	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-8B *	11.8	25.6	3206±84	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-8C *	12.2	25.6	3316±96	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-8D *	12.2	19.7	-----	None	-	None	-	None	-	None	-	None	-	812	3-3.5 Acidic odor
201-9A	13.0	25.6	2833.5±71.5	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-9B *	11.0	25.6	3038±84	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-9C *	9.8	27.6	1911±84	None	-	None	-	4 blisters	-	4 blisters	-	4 blisters	-	4106	3-3.5 Acidic odor
201-9D *	8.3	14.8	728±84	.72	.35	None	-	None	-	None	-	None	-	812	3-3.5 Acidic odor
201-10A *	2.9	29.5	2533.5±156.5	None	-	None	-	None	-	1 lg. blister	10.85	1 lg. blister	13.7	4106	3-3.5 Acidic odor
201-10B *	-	27.6	1283.5±156.5	None	-	None	-	1 lg. blister	-	1 lg. blister	7.0	1 lg. blister	7.5	4106	3-3.5 Acidic odor
201-10C	-	23.6	984±144	None	-	None	-	None	-	None	-	None	-	812	3-3.5 Acidic odor
201-10D *	2.75	31.5	-----	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-11A *	7.5	27.6	2247±84	None	-	None	-	None	-	1 lg. blister	-	1 lg. blister	18.5	4106	3-3.5 Acidic odor
201-11B *	10.6	19.7	3380±96	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-11C *	7.5	29.5	3206±84	None	-	None	-	None	-	None	-	None	-	4106	3-3.5 Acidic odor
201-11D *	11.02	21.65	-----	None	-	None	-	None	-	None	-	None	-	812	3-3.5 Acidic odor
201-12A *	None	35.4	2079±84	None	-	None	-	None	-	Many blisters	-	Many blisters	-	4106	3-3.5 Acidic odor
201-12B *	None	19.7	478±48	1.12	1.0	None	-	None	-	None	-	None	-	1200	3-3.5 Acidic odor



Average Coating Thickness (mils) Gelcoat Coating

Figure 39. Average Blister Initiation Time vs. Average Total Coating Thickness (Coating Gelcoat), for Series 201 at 65°C.

ortho/ortho panel (see Fig. 21). Microscopic observation from series 201, show that the depth of the blister position is more or less identical for those samples without coating.

Most importantly, figure 39 shows that if the combined coating and gel coat thickness had all been gel coat, the blister initiation time would have been sooner. Only samples with coating 10 do not show this. The added protection a coating gives must therefore be the difference between the point the coating represents on Line 2 in Figure 39, and the point of equivalent gel coat thickness on Line 1.

Table seven summarizes for each coating, samples a - c, the average combined gel coat and coating thickness, average blister initiation time, blister initiation time for equivalent gel coat thickness, using equation 9.1, hours of added protection (blister initiation time minus the calculated time using equation 9.1) and relative rating of the coating (1 (best) - 12 (worst)).

In general, for equivalent thickness of coating, coatings 1, 2, 3, 6, and 11, all giving about the same added protection, performed best and coatings 7 and 9, both about the same, gave the poorest added protection. Coating 10 is difficult to evaluate since it washes away with time. No negative effects were apparent.

Microscopic observations from a selected group of samples from each coating set, except coating 7, show that the susceptible site for blister formation is near the chop/veil reinforced zones interface, in the veil zone or at the veil/roving interface. This is approximately 2 mm below the bottom of the gel coat or 3 -4 mm from the back side of the sample. This is described in Section 9. It is clear that coating over a gel coat, with these coatings, does not alter the blister position. Samples with coating 7 developed some blisters in the typically susceptible zone, but predominantly in the chopper glass reinforced zone, just beneath the gel coat. Results from samples series 200 and 202 indicate that some species (s) in the urethane-epoxy blend based

Table 7

Calculated Added Protection Against Blistering for Series 201 at 65°C Gained From the Coating

Coating Number	Average Coating Thickness (gel coat & coating) (mils)	Average Blister Initiation Time (hrs)	Blister initiation time for gel coat of Equivalent Thickness (hrs)	Hours of added protection (hrs)	Rating of coating
1	27.9	2290.3	1305.6	984.7	5
2	24.8	2334.2	981.1	1353.1	1
3	26.4	2342.3	1145.1	1197.3	2
4	26.7	1769.8	1179.2	590.6	8
5	28.2	1958.3	1333.0	625.3	7
6	38.1	3525.8	2351.0	1174.8	3
7	31.4	1909.3	1660.9	248.4	10
8	34.3	2625.2	1958.2	667.0	6
9	37.5	2610.5	2289.5	321.0	9
10	32.4	1600.3	1763.4	-163.1	12
11	34.1	2946.3	1941.1	1005.2	4
gel coat	24.9	970.7	970.7	0	11

coating, diffuses through the gel coat, into the laminate, interacting with some leachable constituent in the laminate, to make the zone highly susceptible to blistering. This interaction most likely forms some water soluble material. The pH of all blister fluid was between 3 and 3.5 which is typical.

Microscopic observations of thin cross-sections showed that the polyester/coating bond was good with all coatings except with antifouling paint (coating 10) and coal tar epoxy (coating 9). Coating blisters formed, to some extent in all coatings, except coatings 7 and 10, epoxy-urethane blend and antifouling paint, respectively. The most extensive coating blisters occurred with solvent based coatings which commonly form coating blisters. These include bottom paints (coatings 1, 2 and 4), marine phenolic spar varnish (coating 3) and coal tar epoxy. Coating 3 only formed a few tiny coating blisters. It did, however, show extensive deterioration. Coating 10, antifouling paint, also degraded after a period of time. This, however, is the property of an antifoulant paint. Coatings 5, 6, 8 and 11 developed some swelling blisters and coating blisters but not very extensively. In some cases what appeared to be coating blisters at first, such as in coating 8, were found to be swelling blisters (See section 10 later).

Debris, left over from sanding between coats, results in bad adhesion between the coats and may lead to coating blisters. Despite the effort to clean the surface after sanding, a substantial amount of debris remained. This is best seen with the clear coatings. Figure 40 shows a photomicrograph of the debris between coats of coating 11. Debris between coats was also seen in coating 8 and the primer coating of coating 6. The debris, however, appeared not to alter the bond between the coats. The particles appear to be watted very well by the coating.

Interestingly, disk cracks formed in coating 11, a penetrating epoxy. These may have been the cause of the coating blisters formed in this coating. Under crossed polarized light, it can be seen that there is a high amount stress in the cured coating. This may have led to the disk cracking.



Figure 40. Photomicrograph Showing Debris Between Coats of Coating 11.

Shrinkage during cure, as well as to a lesser degree, swelling as a result of water permeation, are the probable causes.

Particularly with solvent based coatings, the coating blisters grow very large and eventually break open. This, eventually, can lead to the deterioration and peeling off of the coatings. Surprisingly, no negative effects on blister resistance were seen that could be attributed to coating breakdown.

14.4 Series 202 - Coating in Place of a Gel Coat

Thirty-three samples were chosen randomly from the large orthophthalic acid based gel coat and laminating resin panel described previously. The gel coat was removed using a disk sander. The samples were scrubbed with water to remove any sanding debris. They were dried at ambient room conditions.

Coatings were applied following the procedures listed in Table 5 for each coating. However, in order to compare the performance of a coating to that of a gel coat, a 20 mil wet coating thickness was desired. For this reason, double the manufacturer recommended number of coats were applied. The thickness of each coat was measured using a mil gauge. When using paints, the total dry thickness was considerably below a gel coat thickness.

All samples were totally immersed in 65°C water and monitored for blister initiation time, blister severity, coating blisters, deterioration, etc.,. Once testing had been completed the dry coating thickness was measured for each of the samples. Blister fluid pH was measured. Thin cross-sections were made from a selected group of samples for use in microscopic studies.

Results from Series 202

Results for series 202 samples are presented in table 8.

Table 8. Results for Series 202 - Coating in Place of a Gel Coat, at 65°C

Sample #	Coating Thickness (mils)	Gel Coat Thickness (mils)	Blister Initiation Time/hrs	1 Month		2 Months		Total Immersion Time/hrs	Blister Fluid pH
				Blister Density (Blister/Cm ²)	Max Blister Size (Cm ²)	Blister Density (Blister/Cm ²)	Max Blister Size (Cm ²)		
202-1A	7.0	None	70.0±23.5	2.48	0.08	5.12	0.08	1515	-
202-1B	7.0	None	70.0±23.5	2.48	0.08	3.20	0.06	1515	-
202-1C	6.5	None	118.0±25.0	3.76	0.08	4.96	0.18	1515	-
202-2A	9.1	None	70.0±23.5	None	-	0.8	0.35	1515	4-4.5
202-2B	8.5	None	70.0±23.5	None	-	0.48	0.10	1515	4.0
202-2C	3.1	None	34.0±12.5	None	-	0.96	0.24	1515	-
202-3A	5.1	None	179.0±35.5	Several Blis.	-	0.64	0.16	1515	-
202-3B	4.8	None	179.0±35.5	Several Blis.	-	0.80	2.65	1515	-
202-3C	6.4	None	179.0±35.5	Several Blis.	-	0.32	0.98	1515	-
202-4A	7.8	None	1154.0±95.0	None	-	4 Blisters	0.32	1515	-
202-4B	6.9	None	1382.0±133	None	-	3 Blisters	0.90	1515	-
202-4C	5.4	None	1382.0±133	None	-	4 Blisters	2.38	1515	-
202-5A	8.8	None	503.5±72.5	7.92	0.10	8.08	0.80	1515	-
202-5B	10.5	None	503.5±72.5	11.44	0.14	7.76	0.60	1515	-
202-5C	9.8	None	503.5±72.5	5.92	0.32	8.96	1.60	1515	-
202-6A	Topcoat 13.3 Bottomcoat 13.7	None	599.0±98.0	0.32	1.20	-	-	1153	-
202-6B	Topcoat 11.3	None	599.0±98.0	0.48	0.60	-	-	1153	3-3.5
202-6C	Bottomcoat 12.0 Topcoat 12.1 Bottomcoat 15.2	None	792.0±95.0	0.88	0.08	-	-	1153	3-3.5
202-7A	13.6	None	34.0±12.5	1.52	4.52	2.00	6.25	1515	4.5
202-7B	15.0	None	34.0±12.5	1.12	3.60	1.84	6.48	1515	4.5-5
202-7C	12.8	None	34.0±12.5	1.84	4.52	1.84	6.00	1515	-
202-7D	11.8	None	12.5±12.5	1.60	3.59	-	-	675	-
202-7E	11.1	None	12.5±12.5	2.08	4.4	-	-	675	5.0
202-7F	10.4	None	12.5±12.5	2.40	7.36	-	-	675	5.0
202-8A	26.0	None	384.5±13.0	8 Blisters	-	1.44	2.55	1515	-
202-8B	25.6	None	503.5±72.5	1 Blister	-	1.60	0.35	1515	-
202-8C	25.3	None	503.5±72.5	4 Blisters	-	1.68	2.88	1515	3.5
202-9A	28.5	None	70.0±23.5	None	-	None	-	1515	-
202-9B	19.7	None	503.5±72.5	None	-	None	-	1515	-
202-9C	15.7	None	503.5±72.5	None	-	None	-	1515	-
202-11A	24.4	None	503.5±72.5	2 Blisters	-	1.12	5.06	1515	2.5-3
202-11B	23.7	None	623.5±47.5	1 Blister	-	0.72	3.36	1515	3
202-11C	21.6	None	503.5±72.5	1 Blister	-	0.64	2.94	1515	-

In order to make a comparison for blister resistance among the coatings and to compare them to a gel coat, once again the blister initiation times must be normalized to coating thickness. Although the wet coating thickness was targeted to 20 mils, shrinkage during cure varied significantly among the coatings and created substantial variations in dry coating thickness.

The average blister initiation time vs the average coating thickness, for each of the coatings, is shown in Figure 41. The average was taken for the three samples used to test each coating.

A difficulty that arises for this series is how to normalize the data. Normalizing the data using equation 9.1 becomes meaningless in the absence of the gel coat. Microscopic observations of thin cross-sections show that, for samples with coatings 6, 7, 8 and 11, the blisters are situated in the chopper glass reinforced zone, closer to the coating/laminate interface and with coating seven they are almost at the coating interface. Samples with coatings 1, 2, 3, 4, 5 and 9 have blisters positioned in the typical place for samples from this test panel close to the chop/veil interface. Because of sanding approximately 1 mm of the chopped glass reinforced zone was removed. As a result all blisters become closer to the coating. This reduces the distance the permeating water must travel to sites susceptible to blistering. For this reason equation 9.1 can no longer be used to normalize the coating thickness. Past data, however, has shown that, with blisters found just beneath the gel coat, near the gel coat/resin interface, that if the gel coat thickness is doubled, the blister initiation time roughly doubles. Because these blisters are positioned close to the coating/laminate interface, this assumption will be used for series 202 samples.

Point 1, from figure 21, is the blister initiation time for a blister positioned just beneath the gel coat. Using the above assumption, the relationship between blister initiation time and gel coat thickness becomes

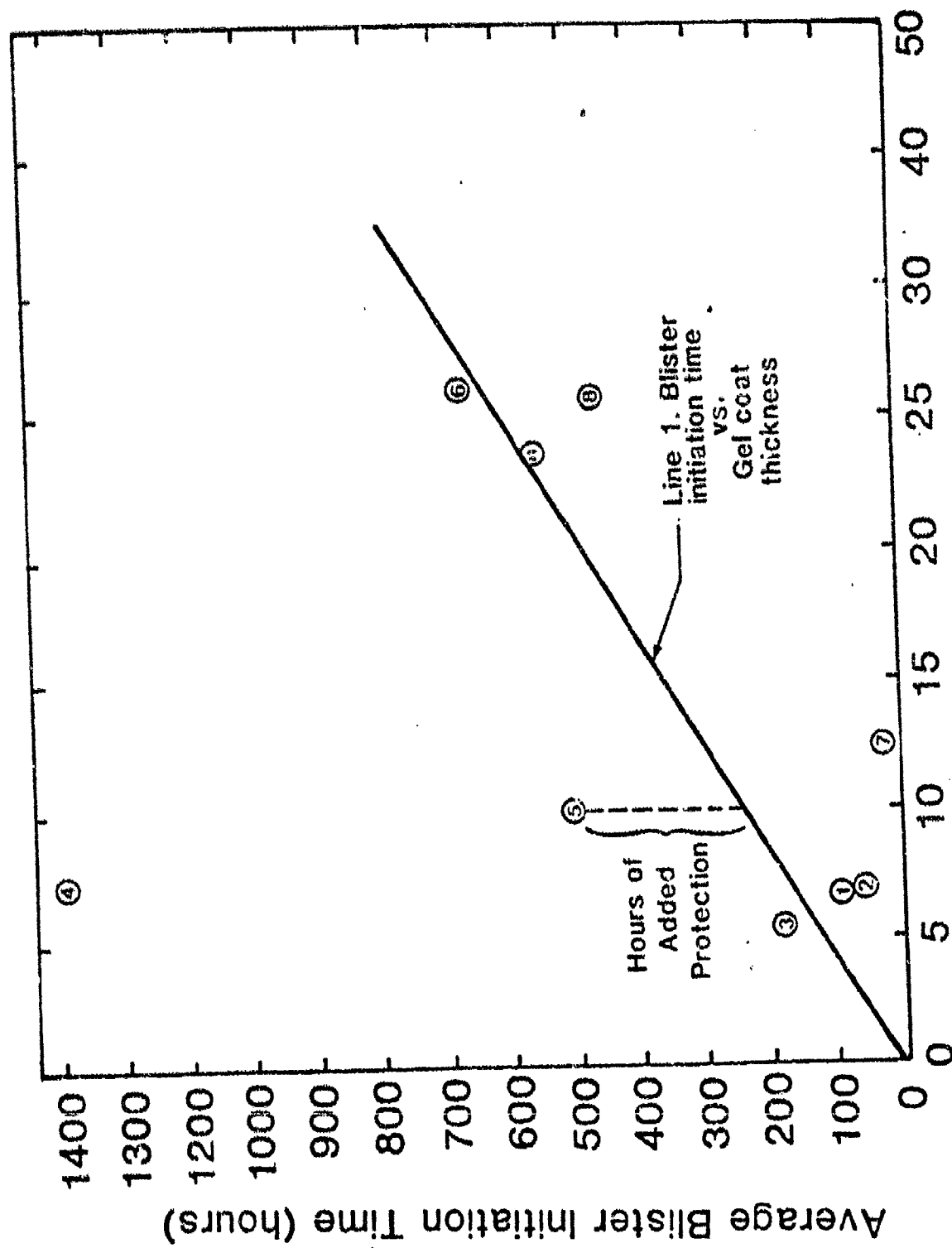


Figure 41. Average Blister Initiation Time vs. Average Coating Thickness

Blister initiation time = $24.3 \times$ gel coat thickness (14.1). This is plotted as line 1 on Figure 41.

Table 9 presents the average coating thickness, average blister initiation time, blister initiation time for equivalent gel coat thickness, using equation 14.1, added protection and relative rating of coating (1 best -11 worst).

Coatings 3, 4, 5 and 6, per equivalent thickness of gel coat, provided added protection against the onset of blistering. All other coatings gave less protection than a gel coat of equivalent thickness. It should be noted that samples with coatings 1, 2, 3, 6 and 11 are plus or minus one hundred hours of blister initiation time for gel coat of equivalent coating thickness. These coatings can be assumed to perform comparably to a gel coat of equivalent thickness. Significant protection against blistering was lost with coatings 7 and 8. On the other hand, coating 4, an urethane-silicone-alkyd based bottom paint, showed superb protective properties against the formation of sub-coating blisters. Coating 5 also gave enhanced added protection.

In this experiment it was very difficult to differentiate coating blisters and swelling blisters from sub-coating blisters. Many times the only way to differentiate the three is by cross-sectioning and examining the sample under a microscope.

Following cross-sectioning of samples with coating 5, those that appeared to be blisters were found to have swollen zones. These swollen zones appear as lines which follow glass fibers when viewed from the surface. One reason for this may be due to polyurethane wetting the loose glass fibers on the surface. As water permeates into the polyurethane coating it swells. This includes any polyurethane surrounding glass fibers. As it swells, it pushes the glass fibers in the bundle apart. This was observed on samples with coating 1 as well, but to a much lesser extent. Fortunately these formed at a later date than sub-coating blisters. Another possible cause for the formation of this type of swelling blisters may be that something on the glass

Table 9. Calculated Added Protection Gained from the Coating against Blistering for Series 202, at 65°C

Coating Number	Average Coating Thickness (mils)	Average Blister Initiation Time (hrs)	Blister Init. time for gel coat of equivalent thickness (hrs)	Hours of Added Protection (hrs)	Rating of Coating
1	6.8	86.2	166.0	-79.8	7
2	6.9	58.0	167.7	-109.7	8
3	5.4	179.0	132.0	47.0	4
4	6.7	1306.0	162.8	1143.2	2
5	9.7	503.5	235.7	268.0	3
6	25.9	663.3	628.8	34.5	5
7	12.4	23.2	302.6	-280.3	10
8	25.6	463.8	622.9	-159.1	9
9	21.3	---	---	---	1
11	23.3	543.5	564.6	-21.1	6

fiber reacts with the polyurethane and causes it to swell with water.

Microscopic cross-sections showed that blister initiation times, for samples with coating 6, an epoxy, were found to be for swelling blisters. What were believed to be blisters in samples with coal tar epoxy, coating 9, later were found to be coating blisters. Sub-coating blisters, that formed never developed enough osmotic pressure to cause the sample to bulge outward. Quite a few swelling blisters formed in coating 8 that were reported to be blisters.

In some cases there is a question of whether the blister initiation times reported are for sub-coating or swelling and/or coating blisters. All blister initiation times were corrected except for samples with coating 9 where it was not possible. These blisters never developed enough osmotic pressure to bulge outward.

Samples with alkyd or alkyd containing bottom paints, coatings 1, 2 and 4, performed surprisingly well when normalized to thickness. Blister severity was much less than with coatings 6,7,8 and 11. Coating 4, a urethane-silicone-alkyd blend performed especially well. Alkyd enamels have been suggested to have poor resistance to water permeation, swelling and coating blister formation. These samples formed coating blisters in a short period of time. With some of these coatings, many coating blisters grew so large that they burst. As a result it would be anticipated that the coating would lose its protective properties. All blisters formed at or near the chop/veil interface. Most did not develop enough osmotic pressure to produce a bump on the sample surface. The reasons that can be given to explain the performance of these alkyd type based coatings are: (1) leaching of water soluble material, (2) stresses produced at the coating/substrate interface were less and (3) some chemical reaction or interreaction between some constituent in the coating with the polyester resin and/or glass.

The coating, while reducing the rate of water permeation into the hull, also does not allow the leaching of water soluble material out. Once the

coating breaks down leaching becomes permissible. Low molecular weight material is necessary for blister and disk crack formation. Disk cracks, however, promote water soluble material leaching. Disk crack and blister formation must precede any substantial leaching and therefore this must be ruled out as one possible explanation.

Microscopic observations of samples with coatings 1, 2 and 4 show no birefringence or stress near the coating/laminate interface. These coatings bond very well to polyester resin, but not to exposed glass fibers. This was the cause of the coating blisters that formed at the interface.

It must therefore be concluded that some chemical interaction or reaction occurred between some constituents(s) in the bottom paint and something in the laminate to reduce the rate of water permeation into the hull and/or to tie up low molecular weight species.

Coating 3, phenolic resin based spar varnish, performed in a similar manner as the bottom paints except that not very many coating blisters developed. However, after a period of time the coating began to degrade.

The polyurethane based coating performed very well. A few blisters formed near the chop/veil interface. None of the blisters generated enough osmotic pressure to cause a bulge on the surface. The surface was, however, covered with a glass pattern that appeared to be swollen zones that follow glass fibers. Very few coating blisters were present. Some did occur at the interface because the polyurethane does not bond well to glass fibers that are exposed on the surface. Except for the epoxies, this coating maintained its surface appearance best and underwent the least, if any, amount of degradation.

Mixed results were obtained with the various epoxies tested. Coatings 6 and 11 gave protection against blistering that is comparable to a gel coat of equivalent thickness. Protection against blister initiation was lost with coatings 7 and 8. Since the blisters produced in samples with coating 9 never

developed enough osmotic pressure to produce a bump on the surface, blister initiation times could not be obtained. The blisters occurred near the chop/veil interface. Many large coating blisters formed and collapsed. This coating absorbs an appreciable amount of water. Water can be squeezed out of the coal tar epoxy. But overall, the coating's protective properties appear to be good.

Samples with coatings 6, 7, 8 and 11 show a shift in blister position. From predominantly being near the chop/veil interface, usually in the veil reinforced zone, the blisters shifted to the chopper glass reinforced zone, close to the coating/laminate interface. Blisters in samples with coating 7 almost formed right at the interface. Several reasons can be hypothesized to explain the performance of these coating:

1. Stresses--Epoxy coatings bond excellently to both polyester resin and glass fibers. Samples with coating 11 appeared to be slightly stressed, when viewed under cross-polarized light, in the chopper glass reinforced zone, just beneath the coating. A substantial amount of stress was present in the coating. Differential swelling, with water absorption, between the epoxy and polyester could increase the stress further at the interface. Stresses can be ruled out as the cause of blistering given the following three reasons: One, samples with coating 11 in series 200 show similar stresses at the coating/substrate interface, but the blisters are positioned at the chop/veil interface. Two, coating 11 was poured over a thin polyester film. Following cure no shrinkage stresses were evident. If such stress had been present it would have caused the sample to bow. Finally, three, no stresses were seen at or near the coating substrate interface with any of the other coatings.

The degree of stress in the coating appears to be a function of the number of coats applied. The stress produced is far greater in samples 202-11A-11C, where 6 coats were applied. Once exposed to water, these stresses are significant to cause disk cracking in the coating. This would alter the protective properties of the coating. Other coatings could not

be evaluated for stresses because of the presence of filler. Fillers may in fact act as reinforcement and may prevent disk cracking.

2. Epoxy/polyester resin interaction. Samples with coating 6, 8 and 11 formed a brownish discolored zone, just beneath the coating, in the chopper glass reinforced zone, approximately 1 mm thick. This zone discolors after approximately one week of exposure to water at 65°C. This is believed to be a result of some constituent in the epoxy based coating diffusing into the polyester resin. Once it interacts with water, a brownish discoloration results. Microscopic examination, under cross polarized light, showed no stresses related to this diffusional layer. Stresses would be a result of swelling. No evidence of a diffusional layer was present in samples that had never seen water. Blisters developed near the brownish discolored zone and the unaffected zone interface. It is not fully clear at this time if there is a connection between the two. In any event, samples with identical coatings in series 200 formed blisters near the chop/veil interface where this same phenomenon was seen. It should be noted that because of the amount of material removed in the repair process, the discolored zone often extended to the chop/veil interface. It is not known how this diffusional layer affects water permeation into the laminate.

3. Low molecular weight material. The final explanation for the change in blister position is the following. Whatever diffuses into the polyester resin, from the uncured epoxy coating, is a source of low molecular weight or it interacts with something in the resin or on the glass fibers to become a source of water soluble material(s).

No diffusional layer developed in samples with coating 7, a urethane-epoxy blend. Blisters were positioned virtually at the coating/laminate interface and initiated overnight on all six samples. After approximately one week of exposure to 65°C water, the entire surface was covered with large blisters. The epoxy blend bonded excellently to both the polyester resin and glass fibers. No stresses were evident. Again, in samples with

this coating in series 200 blisters formed near the chop/veil interface. Sample series 200 were subject to a significant amount of leaching before coating. It is strongly believed that some constituent diffuses into the polyester resin and interacts with a leachable constituent(s) to create a zone that is highly concentrated in water soluble material. The pH of blister fluid was measured between 4.5 and 5.0 with coating 7. All other samples in this series had blister fluid pH's between 3 and 3.5.

14.5 Sample Series 200 - Coatings used as Repair Materials

Sample preparation techniques for samples from series 200 are discussed in Section 15, Evaluation of Repair Techniques. All samples that were used to evaluate coating materials had the gel coat removed by disk sanding. Prior to sanding, all blisters were circled and traced onto a 4" X 4" piece of tracing paper in order to see if blisters will reoccur in those areas once repaired. They were then scrubbed with a stiff brush and water and then immersed in distilled water at room temperature for one week. Each day the samples were scrubbed, the distilled water was replaced and the samples were re-immersed. The samples were dried in a circulating oven, at 65°C, till constant weight readings were obtained.

All samples were coated using the procedures described in Table 5. In addition, three sets of samples were set aside to study the effects of various fillers on blistering. These fillers are commonly used in puttying and fairing compounds. Those tested were phenolic microballoons, glass microspheres and fumed silica. 22.2 percent by volume of filler was added to coating number 11. Otherwise, all manufacturers recommended procedures were followed. Results for the fillers are reported in section 15 which discusses the evaluation of repair techniques.

All samples were immersed in distilled water at 65°C and were monitored periodically for blister initiation, severity and any other notable changes. Following experimentation, the blisters were circled and traced onto the

identical piece of tracing paper to determine if the blisters formed in previously blistered zones. Coating thickness was measured from a section of each of the samples. Blister fluid pH was measured. A selected group of samples were cross-sectioned using a diamond saw later to be used for microscopic examination.

14.6 Results from Series 200

The results for samples used to evaluate coating materials from Series 200 are given in Table 10. Table 11 presents average coating thickness, average blister initiation time and average blister protection per coating thickness.

By tracing blisters prior and after repair, it was found that on all the samples, some blisters did reoccur in previously blistered zones, particularly where large blisters were present before repair. Because most of the blisters were positioned 2mm below the gel coat, during sanding, unless it was known that a blister was there, some blisters could be easily missed. Following repair, once water reaches the blistered site, osmosis will begin again. Similarly, if all the damaged material is not removed entirely, blisters will begin at that site. It is not known if those blisters that initiated first are those that formed in previously blistered zones. Also, during the sanding process, blister fluid smeared many times over the entire sample. If the surface is not properly washed off blisters can develop in that area. Therefore, it is the job of the coating to retard water permeation into the hull and hence to delay the initiation or further growth of blisters.

Prior to repair, all samples from series 200 were exposed to distilled water, at 65°C, for approximately 1896-5136 hours, which is equivalent to 3.6-9.7 years of exposure to water at 25°C (assuming that with every 10°C, the rate of reaction roughly doubles). This was done to create the blister condition desired for repair. Following testing of the repair samples, they were immersed a total of 2484-6644 hours at 65°C or an equivalent of 4.5-12.6 years at 25°C.

Table 10 Results for Series 200 - Coating as a Repair Material, at 65°C

Sample #	Coating Thickness (mil)	Blister Initiation Time (hrs.)	1 Month		2 Months		Total Immersion Time (Hrs.)	Blister Field Ph
			Blister Density (Blister/Cm ²)	Max Blister Size (Cm ²)	Blister Density (Blister/Cm ²)	Max Blister Size (Cm ²)		
200-1A	5.61	255±37	.72	0.12	1.28	.12	1376	-
200-1B	3.26	131±36	4.64	1.5	-	-	1040.5	-
200-2A	5.51	72±23	.32	.21	.4	.08	1376	-
200-2B	3.69	37±12	.96	.36	-	-	1040.5	-
200-2C	3.94	72±23	.08	.45	.25	.6	1376	Acidic Odor
200-3A	4.92	1208.5±167.5	None	-	.16	.09	1376	-
200-3B	-	-----	-	-	-	-	1040.5	-
200-3C	6.17	716±84	None	1.2	-	-	1040.5	-
200-4A	5.27	584±48	Few blisters	.12	.48	.12	1376	-
200-4B	5.71	716±84	None	2.1	-	-	1040.5	-
200-5A	5.84	363±24	.88	.45	1.04	.35	1376	-
200-5B	5.91	488±48	1.36	.2	.4	0.48	1376	-
200-5C	5.12	488±48	.48	2.55	-	-	1040.5	-
200-6A	Topcoat 6.4	60±12	2.48	.25	-	-	1152	3.0
200-6B	Bottomcoat 8.5	60±12	4.72	1.9	-	-	1152	-
200-6C	Topcoat 5.8	60±12	4.64	0.48	-	-	1152	-
200-6D	Bottomcoat 6.5	488±48	Several tiny blis.	.07	Few blisters	.09	1376(65°C)	-
200-6E	Topcoat 6.0	>1376	None	-	None	-	315(80°C)	-
200-6F	Bottomcoat 9.9	131±36	0.32	.36	.4	2.55	1376(65°C)	-
200-7A	9.8	225±12	1 Blister	3.48	1.28	14.7	1508	3.0
200-7B	6.8	404±36	1 Blister	4.60	1.04	10.5	1508	3.0
200-7C	9.7	129±36	0.80	1.04	1.28	3.4	1508	-
200-8A	14.1	129±36	Some Small Bls.	-	8.72	0.2	1508	-
200-8B	15.4	189±24	Some Small Bls.	-	4.64	0.28	1508	-
200-8C	16.7	129±36	2 Blisters	-	3.20	3.0	1508	Acidic Odor
200-9A	9.3	763±95	None	-	1.36	1.32	1508	-
200-9B	14.8	763±95	None	-	1.36	3.23	1508	-
200-9C	10.9	763±95	None	-	2.48	0.4	1508	-
200-11A	11.6	763±95	None	-	1.52	4.62	1508	Acidic Odor
200-11B	10.9	584±84	2 Blisters	-	1.36	7.13	1508	3.0
200-11C	10.3	584±84	Few Blisters	-	1.52	5.46	1508	3.0

Table 11 Summary of Results for Coating Materials Used as Repair Materials.
Series 200, at 65°C

Coating Number	Average Coating Thickness (mils)	Average Blister Initiation Time (hrs)	Protection Against Blistering per Coating Thickness (hrs/mil)
1	4.4	193.0	43.6
2	4.4	60.3	13.8
3	5.5	962.0	173.6
4	5.5	650.0	118.4
5	5.6	446.3	79.4
6	14.4	792.0	55.0
7	8.8	240.7	27.4
8	15.4	703.5	45.7
9	11.7	---	---
11	10.9	643.7	58.9

Excluding the chopper glass reinforced zones, these samples are severely disk cracked from the veil mat reinforced zone to the back side of the sample. Susceptibility of this zone to blistering is discussed in Section 9. Disk cracks provide a gateway for low molecular weight species to leach out. Leaching does take place without disk cracking but the process is extremely slow.

Because of the long time the samples were exposed to water, it is believed that a significant amount of leaching had taken place. A reduction in the availability of water soluble constituents could lengthen the time for blisters to initiate, reduce severity and reduce the rate of blister growth. Even though roughly half the coating thickness applied in series 202 was used in series 200, generally speaking, the blister initiation times were increased in series 200.

Microscopic observations show that all blisters are positioned near the chop/veil interface. This is where most all blisters were positioned prior to repair. Because variable amounts of laminate were ground off across a sample in order to remove all damaged material, the chop/veil zone becomes located at variable distances from the coating. This affects blister initiation times. This is one reason why the performance of the coatings cannot be compared to that of a gel coat.

As expected, there is a general increase in blister initiation time with increasing coating thickness. Samples with coatings 3 and 4, phenolic spar varnish and urethane-silicone-alkyd blend bottom paint, respectively, gave the best added protection against blistering per mil thickness of coating. The worst protection per thickness is given by coatings 2, silicone alkyd enamel and 7, urethane-epoxy blend based coating. Again, coating 9 could not be evaluated since large coating blisters formed on the surface, but no sub-coating blisters were observed. Blisters were only found following cross-sectioning. Coating 2 performed as well as a gel coat in series 202 and better than a gel coat in series 201. The reason for its poor performance in this series is not known. The types of hull damage produced in samples with

coatings 1, 2, 3, 4, 5 and 9 were predominantly blisters that were in the form of osmotic cracks. Most never developed enough osmotic pressure to create a visible bump on the surface. They were fewer in quantity and smaller in size than those produced with coating 6, 7, 8 and 11. These blisters appear identical to or slightly worse than those produced with new gel coated samples. The blisters bulge outward and are large. This signifies that a substantial amount of osmotic pressure is being generated.

A very thin brown diffusional layer formed beneath coating 9, while a fairly thick layer, approximately 1mm, formed in samples with coatings 6, 8 and 11. Most all blisters were adjacent to or in the brown diffusional layer and were near the chop/veil interface.

Blisters in samples with coating 7 were positioned near the chop/veil interface. To the contrary, samples coated with coating 7 in series 202 formed blisters almost at the coating/substrate interface. This signifies that some interaction of the laminate with some diffusing species from the uncured epoxy generates osmotic centers.

Severe coating blisters occurred in coating 2, to a lesser degree in coatings 4 and 9 and very few were seen in coatings 1, 3 and 11. Swelling blisters were found in coatings 5, 6 and 8. No defects were found in coating 7. In some cases, coating and swelling blisters were mistaken for sub-coating blisters when reporting blister initiation times and severity. All data was corrected, except for coating 9 results where it was not feasible. During testing, no blisters were visible in the three samples.

Basically two types of coating-blisters were found--those produced at the coating/substrate interface and those produced between coats. Those formed at the interface are a result of a poor bond between the coating and substrate. With coatings 1, 2, 3, 4 and 5, they appear to be a result of a poor bond with glass fibers. All epoxies bonded very well to glass. All of the coatings, except coating 9, formed an excellent bond with polyester resin. Coating 9 fell off during machining, indicating a fairly weak bond.

14.7 Series 203 Evaluation of Repair Materials on a
Severely Blistered Boat Hull

Procedures

The procedures used are identical to those followed for the evaluation of repair material for series 200.

Results

Initially, an attempt was made to make a record of all blisters, prior to repair, by tracing them onto a 4" X 4" piece of tracing paper. But since the entire boat hull panels were blistered, it was felt that no information would be gained by tracing the blisters.

No blisters ever formed in the coated samples. Initially it was thought that blisters were present in those samples with coating 6. Following microscopic examination, these were found to be swelling blisters. In all coatings, except coating 7, swelling and/or coating blisters were present to some extent.

The reason for the absence of blisters is attributed to a substantial leaching of low molecular weight material from the laminate. The boat panels were substantially blistered upon receipt. However, because all blisters had dried out and collapsed, the boat hull, after it was cut into small panels was immersed in 65°C water in order for the blister cavities to refill with fluid once again. The panels were soaked for a long period of time. During this period, more blisters developed and most blisters cracked open. Eventually the entire gel coat was cracked. This allowed all blister fluid, concentrated in low molecular weight constituents, to flow out and leaching from the surrounding resin to become more rapid. During the repair process, the samples were soaked and periodically scrubbed in distilled water for one week,

thus allowing further leaching to take place.

It can be concluded from this study that leaching is a very important phenomenon. Once low molecular weight constituents are removed from a boat hull it will not disk crack or blister. These findings offer considerable hope for the repair of severely damaged hulls. It should be emphasized that the restoration of such a hull must be more than just a coating procedure. Considerable strength loss accompanies severe blistering. Additional layers of fiberglass must be placed over the hull in order to restore strength. Coatings then can be added to prevent blistering.

14.8 Summary of Coating Results

Table 12 summarizes the results from series 200, 201 and 202. Table 13 presents blister initiation times, from all three test series (excluding series 203), if the experiments had been conducted at 25°C instead of 65°C. It is assumed that with every 10°C or 18°F, the rate of reaction, or rate of blistering, roughly doubles. Table 13 provides a better guideline for deciding how well the coatings will delay blistering in a practical situation. Protection per thickness of coating is very important. But since the manufacturer's recommended number of coats or thickness should always be followed, it is more practical to evaluate the coatings' performance per manufacturer's recommended thickness. Adverse effects could arise with coatings that are too thick, particularly with those coatings that cure or dry by solvent evaporation. However, no negative effects were observed with the coatings in series 202 where double the manufacturers' recommended number of coats were applied.

One advantage to epoxies is the ability to achieve thick coating films. The thicker the coating, the longer it takes for water to permeate into the underlying laminate and the longer it takes for blisters to initiate. But normalized to thickness, their protective properties are no better than that of the gel coat's, when coated over an un-gel-coated laminate, and in some

TABLE 12. SUMMARY OF RESULTS FOR COATING MATERIAL AT 65°C

Coating Method	TEST SERIES 200				TEST SERIES 201				TEST SERIES 202			
	Blister Initiation Time (hrs)	Coating Protection (hrs)	Blister Position	Coating Protection (hrs)	Blister Initiation Time (hrs)	Coating Protection (hrs)	Blister Position	Coating Protection (hrs)	Blister Initiation Time (hrs)	Coating Protection (hrs)	Blister Position	Coating Protection (hrs)
1 Alkyd enamel	1700	001	0	0	0	0	0	0	0	0	0	0
2 Alkyd enamel	2200	001	0	0	0	0	0	0	0	0	0	0
3 Epoxy resin	1100	001	0	0	0	0	0	0	0	0	0	0
4 Epoxy resin	1200	001	0	0	0	0	0	0	0	0	0	0
5 Polyurethane	1000	001	0	0	0	0	0	0	0	0	0	0
6 Polyurethane	1100	001	0	0	0	0	0	0	0	0	0	0
7 Epoxy resin	1200	001	0	0	0	0	0	0	0	0	0	0
8 Epoxy resin	1300	001	0	0	0	0	0	0	0	0	0	0
9 Epoxy resin	1400	001	0	0	0	0	0	0	0	0	0	0
10 Epoxy resin	1500	001	0	0	0	0	0	0	0	0	0	0
11 Epoxy resin	1600	001	0	0	0	0	0	0	0	0	0	0

Blister Initiation Time (hrs) Coating Protection (hrs) Blister Position Coating Protection (hrs) Blister Initiation Time (hrs) Coating Protection (hrs) Blister Position Coating Protection (hrs) Blister Initiation Time (hrs) Coating Protection (hrs) Blister Position Coating Protection (hrs)

0 - None 0 - None 0 - None 0 - None 0 - None 0 - None 0 - None 0 - None 0 - None 0 - None 0 - None 0 - None

1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb 1 - 1 lb

00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few 00 - White & few

000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe) 000 - Very many (severe)

C - Chipping glass reinforced B - Blister
 V - Well wet reinforced L - 1 lb
 0/0 - Near chip/fall interface W - None

Table 13. Summary of Blister Initiation Times at 25°C

<u>coat-</u> <u>ing</u>	<u>Series 200</u>		<u>Series 201</u>			<u>Series 202</u>	
	hours	months	hours	months	years	hours	months
1	3088	4.15	36640	49.2	4.1	1376	1.8
2	960	1.3	37344	50.2	4.2	928	1.2
3	15392	20.7	37472	50.4	4.2	2864	3.8
4	10400	14.0	28320	38.1	3.2	20896	28.1
5	7136	9.6	31328	42.1	3.5	8048	10.8
6	12672	17.0	56416	75.8	6.3	10608	14.2
7	3856	5.2	30554	41.0	3.4	368	0.5
8	11248	15.1	42000	56.4	4.7	7424	10.0
9	---	---	41760	56.1	4.7	---	---
10	---	---	25605	34.4	2.9	---	---
11	10304	13.8	47136	63.4	5.3	8688	11.7
12	---	---	15520	20.9	1.75	---	---

cases comparable to bottom paints.

Coating an epoxy over a gel coat will delay the onset of blistering and may in fact reduce blister severity. This is a result of coating thickness and the epoxy's low permeability to water. At 25°C, coating 6 will delay the onset of blistering for 6.3 years, coating 11 for 5.3 years and coatings 8 and 9 for 4.7 years. All others will give 2-3 years of added protection. But in general, any sort of coating will help. The only one not recommended is coating 7, a urethane-epoxy blend. The coating gave added protection, but the blister position was moved to directly beneath the gel coat. In these samples, this zone is normally not susceptible to blistering. If used in a laminate where this zone is already susceptible to blistering, this coating may lead to more devastating results.

If a coating is applied over a bare laminate, coating/polyester resin interactions must be considered. In sample series 202, the epoxies, coatings 6,8 and 11, will delay blistering longer than some of the non-epoxy coatings, but the price one pays is increased blister severity. Many large blisters formed in these samples and the blister position was altered. Epoxies may in fact present a greater problem if the susceptible zone to blistering is already beneath the coating. This is not known without further experimentation. On the other hand, with coatings 1,2,3,4,5 and 9, far less blisters formed and most all never develop enough osmotic pressure to cause a bulge on the surface. However the disadvantage with many of these coatings is poor surface appearance; i.e. coating blisters. Coating 4, a urethane-silicone-alkyd blend bottom paint, gave superb results when used over the bare laminate. Coating 5, a two part aliphatic polyurethane enamel performed very well also. The polyurethane retains its surface appearance very well. The epoxy-urethane blend, coating 7, gave disastrous results.

In samples series 200 the effects of leaching become evident as it plays a role on the performance of the coatings. In this series the coating is placed over the base laminate after blisters have been removed. The epoxy coating performed better here than in series 202. But still, blister severity is

equivalent to gel coated samples and more severe than with coatings 1,2,3,4,5 and 9. Coatings 3 and 4, phenolic spar varnish and urethane silicone-alkyd based bottom paint, respectively, gave excellent protection per mil of coating and per total applied thickness. Coating 7, again, does not give as much protection per mil of coating applied as the other coatings. Severity is similar to that for gel coated samples. To conclude, in most cases epoxy based coating will delay the onset of blistering best because of the ability to achieve thicker films. They can be used with confidence over a gel coat, but with care over a bare laminate, because once blisters do initiate, the size, quantity and rate of growth of blisters will be far greater than with any of the other coatings (except for coating 7).

If an epoxy is to be used, it must be one such that, using the manufacturer's recommended procedures, a thick film of at least 10 mils dry can be achieved. Otherwise, all advantages are lost. Coating 6, a two-part system, with a penetrating epoxy undercoat and a pigmented overcoat epoxy, performed best. Coating 11, a penetrating epoxy, also performed very well.

A bottom paint is highly recommended when coating over an un-gel-coated fiberglass reinforced laminate. Performance is very good over gel-coated samples as well. Overall, the two that performed best were coating 4, a urethane-silicone-alkyd blend bottom paint and coating 5, a two-part aliphatic polyurethane enamel. The polyurethane gave the best surface appearance after prolonged exposure to water. Epoxy-urethane based coating can not be recommended.

In any event, it is obvious that coatings will not prevent blistering if placed on a substrate that contains osmotic centers. At most, if chosen carefully, a coating can significantly delay the onset of blistering and reduce blister severity. The only way to prevent blistering is to keep the fiberglass hull material free from water saturation. This can only be accomplished by removing the coating, drying the hull and then replacing the coating before the hull begins to saturate with water. This should be done well before the blister initiation times reported for each of the coatings in

Table 13. As long as the absorbed water in the hull is kept below saturation, blisters and disk cracks can not initiate.

These recommendations are only based on the experimental results obtained from this study. Blister initiation times may vary with laminates constructed of different materials than those tested here.

15. Evaluation of Repair Techniques

Termination of the blistering process is very important in order to keep the hull structurally sound. The blistering process can be interrupted or terminated by repairing the hull. Repair of a blistered hull is generally very expensive and the hull may re-blister some time later. Each time the hull blisters and becomes damaged some laminate is removed in the process. Unremoved damaged laminate becomes a site for blister growth and hull failure. Eventually the lost material must be replaced. For this reason it is very important to reduce the number of times a hull is repaired. This can be done by finding the best repair materials and techniques.

Repairing a hull usually involves the following:

1. Removal of antifouling and bottom paints and gel coat either from the blistered zone or the entire hull.
2. Removal of all damaged fiberglass reinforced polyester resin. This includes the opening of blisters and removal of all damaged resin adjacent to the blisters.
3. Washing the hull to remove low molecular weight materials that are concentrated in blistered sites.
4. Drying the hull in order to delay the onset of blistering.

5. Filling and fairing of all blistered areas, if necessary, with fairing compounds or reinforced polyester resin.
6. Recoating of the hull to protect it from water absorption and blistering.

Each of these aspects of repair will be investigated to some extent. The following repair procedures will be evaluated:

A. Gelcoat and Damaged Material Removal (coated).

1. (Control) Removal using a disk sander.
2. Removal using heat gun and scraper.

Though sand blasting is a convenient technique, because of its limitations for usage in the laboratory, this procedure was not evaluated.

B. Washing the Hull. The following five methods were evaluated:

(control) 1. Scrubbed with water to remove sanding debris. This is followed by immersion in distilled water at room temperature for one week and scrubbed with water daily. Immersion in distilled water will allow low molecular weight constituents to leach out.

2. Short, light rinse and scrubbed with:

- a) water
- b) mild soap solution
- c) 5 wt. % ammonia in water solution.

3. Short high pressure rinse using a spray gun.

4. No washing, just a light brushing of the surface in order to remove excess debris.

C. Drying of the Hull

(control) 1. Approximately one week in a circulating oven at 65°C. Samples are weighed periodically. Dryness is achieved when constant weight readings are obtained.

2. One week natural drying at ambient room conditions.

3. Two days natural drying at ambient room conditions.

D. Filling and Fairing Combination of an epoxy with one of the following fillers used commonly for filling and fairing:

1. Phenolic microballoons
2. Glass microspheres
3. Colloidal silica
4. Milled glass fibers (only used for permeation study)
5. No added filler

In all cases, 22.2 percent by volume of filler was added to coating 11. Instead of filling individual gouges in the hull samples, the entire sample was coated with the fairing compound. No overcoat was applied. See coating procedures.

E. Coating of the Laminate All coatings listed in Section 14, except for antifouling paint and gel coat, were tested. Gel coat was not tested because of the difficulty of avoiding an air inhibition layer while simultaneously trying to control thickness.

All experimental procedures and results are presented in Section 14. Coating 6 was used as the control for the evaluation of all repair techniques.

In order to evaluate the effect each step in the repair process has on the performance of the sample, all other steps are kept at the designated controls.

Two different laminates were used to evaluate repair procedures. All panels were sawed up into 4" x 4" pieces. The first is the very large panel with an orthophthalic acid based laminating resin and gel coat donated to us by a local boat manufacturer. Seventy-two samples were immersed in distilled water at 65°C till a significant number of blisters had formed. Data taken for the first forty-five of these samples are presented in section 9. Total immersion times varied from 1896 to 5136 hours. Immediately following removal from water, all blisters were circled and traced onto a numbered 4" x 4" piece of tracing paper and filed for later use. Once testing of the repair procedures was completed, blisters on the repaired samples were circled and traced onto the identical piece of tracing paper. This way it can be determined if blisters form in already previously blistered zones. Table 14 presents sample numbers with the repair procedures used.

The second set used to evaluate repair techniques were 17 severely blistered sections from a boat donated to us by a boat manufacturer. The gel coat was isophthalic acid and / neopentyl glycol based. The laminating resin used was isophthalic acid/propylene glycol based, cured with BPO. The entire laminate is reinforced with choperglass roving. The panels have a foam backing which could not be removed entirely.

Because the panels were out of water for an extensive period of time, the blisters had dried out and were very difficult to identify. The boat sections were immersed in 65°C distilled water for some period of time so blister cavities could refill with solution. Many of the blisters cracked open. Eventually the entire gel coat surface cracked. Blister tracing was attempted but since the entire surface was blistered, it became tedious and meaningless. Before repair the panels were cut up into 4" x 4" pieces. Each sample was labeled using the panel number (1-17) and the sample letter from the panel. Sample numbers, with their repair schemes, are listed in table 15.

Table 14. Repair Procedures for Series 200

<u>Sample Number</u>	<u>*Procedure Tested</u>
2, 20, 5a	control
1, 52, 66	B - 3
30, 39, 64	B - 2a
9, 62, 69a	B - 2b
4, 56, 68	B - 2c
11, 36, 45	B - 4
33, 60, 69	C - 3
8, 35, 50	C - 2
3 (11A), 13 (11B), 17 (11C)	D - 5
7 (11-1D), 51 (11-1E), 55 (11-1F)	D - 1
16 (11-2G), 28 (11-2H), 53 (11-2I)	D - 2
42 (11-3J), 46 (11-3K), 63 (11-3L)	D - 3

* All other variables, besides those procedures to be evaluated, are kept at the designated controls. Designations are given in the text.

Table 15. Repair Procedures for Series 203

<u>Sample Number</u>	<u>*Procedure Tested</u>
1B, 3A, 3C, 4A, 4B, 5A, 5E, 6C, 6E	control
2B, 5F, 6F	B - 3
1A, 2A, 6B	B - 2a
5C, 15B, 7A	B - 2b
7F, 9C, 10A	B - 2c
10B, 15A, 16C	B - 4
2C, 5B, 6A	C - 3
3B, 5D, 6D	C - 2
17A, 17B, 17C, 17D	A - 2

* All other variables, besides those procedures to be evaluated, are kept at the designated controls. Letter-number designations are given in the text.

15.1 Results on Repair Techniques

This set of experiments was extremely disappointing in one respect and quite encouraging in another respect. One set of samples (series 203) never blistered so variations in repair techniques could not be evaluated. The second set (series 200) blistered so slowly that the test temperature had to be elevated in order to differentiate one treatment from another within the time frame of the study. The encouraging aspect is that none of the variations in repair techniques caused conditions that destroyed the effectiveness of coating repair procedures.

Series 203 was made using the severely blistered boat hull. When the samples were repaired and testing was begun, we did not realize that all water soluble constituents had been leached from the material and hence it was no longer subject to blistering. Only in panel 17 did large interfacial blisters form. The others showed no blistering after several thousand hours. For these reasons only series 200 results are reported for repair performance. These results are given in table 16.

The following conclusion can be drawn on the various repair techniques tested:

1. Removal of blister damaged material.

This is a very crucial step in the repair process. All blisters and surrounding damaged material must be removed. These sites are concentrated in low molecular weight material. If not removed, once permeating water reaches these zones, blisters will initiate almost immediately since one ingredient for blister formation and growth is already present. In addition, the damaged material serves no purpose since it has no structural integrity. It must be replaced.

Table 16 Results from the Evaluation of Repair Techniques for Series 200 after 1376 hours of Exposure to Water at 65°C

Tested Procedure	Sample Number	Blister Initiation time (hrs)	Blister Density (blisters /cm ²)	Maximum blister size (cm ²)
Control	2	488± 48	few blisters	0.09
	20	>1376	none	---
	59	131± 36	0.40	2.55
B-3	1	488± 48	0.32	0.90
	52	363± 24	0.32	6.60
	66	1208± 68	0.32	11.80
B-2a	30	716± 84	0.40	1.20
	39	1208±168	few blisters	0.49
	64	1208±168	0.32	0.36
B-2b	9	584± 48	0.08	0.60
	62	584± 48	0.56	1.50
	69a	488± 48	0.72	0.35
B-2c	4	488± 48	0.48	0.21
	56	1208±168	0.16	5.75
	68	413± 26	2.00	0.24
B-4	11	>1376	none	---
	36	>1376	none	---
	45	488± 48	0.32	0.36
C-3	33	>1376	none	---
	60	>1376	none	---
	69	1208±168	few blisters	0.20
C-2	8	1208±168	1 blister	3.52
	35	488± 48	0.64	2.00
	50	716± 84	0.80	0.15

Table 17. Results for Series 200 - Evaluation of the Effects of Fillers on Blistering, After One Month Immersion at 65°C

Sample Number	filler	coating thickness (mils)	Blister initiation time (hrs)	Ave. Blister initiation time per coating thickness (hrs/mil)	Blister density (blisters/cm ²)	Blister severity (max blister size cm)	Total immersion time
11A	none	11.6	763±95		none	-	1508
11B	none	10.9	504±34	58.9	2 blisters few blisters	-	1508
11C	none	10.3	504±34			-	1508
11-10	phenolic microballoons	27.7	1208±167	31.1	none	-	1376
11-1E	phenolic microballoons	32.4	1208±167		none	-	1376
11-1F	phenolic microballoons	35.6	561±48		.08	.64	1376
11-2G	glass microspheres	15.7	465±48	32.6	1.28	.84	1048
11-2H	glass microspheres	19.0	541±48		.16	.7	1048
11-2I	glass microspheres	17.1	693±87		.64	.2	1048
11-3J	colloidal silica	16.5	1288±167	67.2	none	-	1376
11-3K	colloidal silica	14.8	1288±167		none	-	1376
11-3L	colloidal silica	13.9	1288±167		none	.2	1048

By making traces of blister positions prior and following repair, it was found that some blisters do recur in previously blistered zones. It is not known, however, if these were the first blisters to initiate since these sites would already be concentrated in low molecular weight material. Most blisters that formed occurred in zones, that prior to repair, never had blistered. Three possible reasons can be given for this: 1) Blisters that never showed on the surface were present in these areas and were not removed while sanding. 2) The material around blistered zones is deprived of low molecular weight material. It is still available in previously unblistered zones. 3) Epoxy coating interacts with some low molecular weight constituent to make the area susceptible to blistering.

In sample series 200, the blisters are positioned approximately 2mm beneath the bottom of the gel coat, near the chop/veil interface. Because of the depth of these blisters, removal of blisters becomes very difficult unless the exact location of the blister on the sample is known. Many blisters could have been missed while sanding.

Removal using a disk sander gives a very smooth surface. Removal using a heat gun and scraper results in an extremely poor surface. This method was only done for panel 17 in series 203. Only the gel coat can be scraped off and this is very difficult. Removal of blister damaged material is impossible. During scraping, glass fibers get torn out of the glass fiber/polyester matrix. The surface is very rough with loose glass fibers extending outward. This leads to interfacial failure between the coating and substrate. Similar interfacial blisters were also seen in sample series 200 where deep blisters were present prior to repair, particularly down the tapered sides of these zones. The pH of this blister fluid is around 5 with epoxy based coatings. These blisters contain many loose glass fibers that are only partially wetted by the epoxy resin. Epoxy resin wets and bonds excellently to glass fibers. It is suspected that air becomes entrapped between the loose glass fibers so that uncured epoxy resin cannot flow in. Also, sanding

debris may get trapped in the fibers.

Coating onto a smooth surface is extremely important in order to avoid interfacial problems. All loose glass fibers should be sanded down.

Removal using a heat gun and a scraper is not advised. Not only because of a poor coating surface, but more importantly because it is extremely dangerous. Polyester resin is extremely flammable. During gel coat removal the laminate caught fire, very quickly, many times. The high heat will alter the properties of the polyester resin as well. The force of scraping may damage the laminate by introducing microcracks.

Sandblasting is commonly used. This technique was not tested since it could not be done in the laboratory. If not done properly it may damage the laminate. The force of sandblasting could produce microcracks in the laminate and imbed low molecular weight material into the laminate. If sandblasting is used, the gun should be held at a low angle to the hull and the size and type of nozzle should be carefully selected.

2. Washing the Hull

Many repairers have suggested that once sanding has been completed, a thorough washing of the hull is necessary to remove low molecular weight material from blistered sites.

Six different washing techniques were evaluated; one week immersion in distilled water; high pressure wash with a nozzle; three types of rinses-- water, soap and water ammonia solution, followed by a fresh water rinse; and no washing, just a dry brushing of the surface. An ammonia rinse would help neutralize blister fluid.

Surprisingly no difference in severity was seen among the six methods. Brushing of debris from the surface was just as effective as immersion in distilled water for one week and brushing daily. By immersing in distilled water at 25°C, it was hoped that low molecular weight constituents would be leached out. The rate of leaching at 25°C is extremely slow.

It is doubtful if any water soluble constituents, in the laminate were removed by washing and soaking. The only way to remove low molecular weight material from blistered sites is by sanding. No damaged material should be left. Scrubbing and rinsing the bare laminate with fresh water to remove all loose debris is highly recommended. During the sanding process, as blisters are ruptured, blister fluid may smear or flow across the laminate. This should be thoroughly washed off. A mild soap and water wash may help loosen debris from the surface, but it must be followed by a thorough rinse with fresh water to remove all soap residue.

Microscopic examination of the laminate surface, using a binocular microscope showed that even with a light rinse, all voids examined were cleaned of sanding debris. Debris left on the surface may lead to poor adhesion of the coating or resin to the underlying laminate. Some interfacial blisters were discovered which were the result of sanding debris left on the surface.

3. Drying of the Hull

Before a laminate is recoated it must be dried. Water is one necessary ingredient for blister formation. As long as water is kept out of the hull, or below the saturation level, disk cracks and blisters will not develop. If a moisture laden hull is coated, the coating will seal the moisture in. If a high concentration of water is already present in the laminate, it will disk crack and re-blister sooner. Hull drying is discussed more thoroughly in section 12.

Three drying schedules were tested; two days and one week of natural drying and complete drying in a circulating oven at 65°C. Before drying these samples were found to contain from 1.2 to 1.42 percent water. From this it can be approximated that the samples that were dried for two days and one week contained .47 to .77 percent water and .17 to .25 percent water, respectively, when coating took place. No apparent effect was evident on blister initiation times among the different treatments. The laminate saturates very quickly with water at 65°C and therefore blister initiation would be dependent on the availability of water soluble material. At 25°C a difference in blister initiation times is expected due to the water concentration difference. However, after coating, the samples were placed in 65°C water. At this higher temperature, a new saturation level will be established. The water concentration at 25°C is much below the new 65°C saturation level.

Results from drying experiments and recommendations are presented in more detail in Section 12.

4. Filling and Fairing

Three types of fillers, commonly used in filling and fairing compounds, were tested for their effects on blistering. Those tested are colloidal silica, glass microspheres and phenolic microballoons. All fillers were added to coating 11, a penetrating epoxy at a concentration of 22.2 percent by volume. Results are presented in Table 17.

Per thickness of coating, colloidal silica has no adverse effect on the coating's protective properties. Those samples with added glass microspheres and phenolic microballoons performed about the same per mil of coating, but had roughly half the protection against blistering than those samples with no added filler. This is in agreement with permeability studies. Though diffusion coefficients are not affected by the type of filler, except with phenolic microballoons where it is almost a magnitude slower, the saturation

levels with these hollow fillers increases four or five fold. This suggests that water is entering these hollow spheres. If saturated water is present on the surface (or interface) of the polyester resin, then the laminate will saturate with water and blister faster.

The surface of coatings containing microballoons and microspheres develop small pits after a short period of time. The hollow spheres on the surface must break away. The epoxy bonds very well to the fillers. Large coating blisters form over the entire surface with the coating containing glass microspheres. These form in between the coats. Many of the glass microspheres appear to be broken. Swelling of the polymer with water absorption will put these hollow spheres into compression. This force must be significant to cause the filler to rupture.

Fairing compounds with hollow type fillers are not recommended. Hollow fillers make the putty sandable, which otherwise may be difficult. If a coating is placed over a hollow filler containing putty once water enters the putty, it may result in failure of the coating and more rapid hull blistering.

From these findings on repair techniques, from results of coating material performance and from discussions with boat owners and repairers, a set of recommendations for repair has been prepared and can be obtained from the American Boat Builders and Repairers Association.

17. Summary of Conclusions

There are so many findings in this report that a complete summary is difficult without repeating much of the report. However, there are several new and important results which should be emphasized and several basic findings which, while previously reported, should be stressed.

1. Blisters result from water interactions with water soluble materials in the laminate.

2. Blisters are initiated at disk cracks and these can form only if the hull material becomes saturated with water. Blisters may form earlier at sites where there is a high concentration of water soluble material.
3. Blistering proceeds from surface levels, down into the hull, as water saturation becomes deeper and deeper. Deep seated "Blisters" show up as osmotic cracks which can lead to hull delamination and loss of laminate strength.
4. Certain coatings or binders on glass fibers were shown to be the major cause of blistering in several laminates.
5. Gel Coats are effective barriers to water build-up in the hull.
6. Because of the wide range of blister initiation times for samples taken from a single panel, blister research is most meaningful if many samples are analyzed statistically.
7. Coating materials used in repair may interact with the hull material. The interaction can promote or retard blistering. Several epoxies showed harmful interactions. Marine paints performed extremely well.
8. The thickness of a barrier coating is a major factor in slowing blistering. Since epoxies can be built to 20 mils, they can be used in repair. However, two coats of an alkyd blend marine paint and a two-part marine polyurethane perform just as well.
9. Three crucial steps for a successful repair of a blistered hull are:
 - (1) the complete removal of blister damaged material, (2) the drying of the hull to 50 percent (or less) of water saturation, and (3) the selection of the coating material.

10. Many boats made with high quality, well cured resins and gel coats and water resistant glass, will not blister.

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