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THE CAUSES OF BOAT HULL BLISTERS

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This report is the product of work accomplished under
U.S Coast Guard Grant #1501.83

Sponsored by American Boat Builders & Repairers Association, Inc.

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by

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16. Abstract

Abstract of "The Causes of Boat Hull Blisters"

This report is a highly-readable and condensed summary of the work undertaken to investigate the causes of blistering in fiberglass reinforced polyester composites, the structural material of many small boats, which are subject to blistering. The report is divided into the following sections: Introduction; How Blisters Form; the Hull Material; Manufacturing Processes; Water Diffusion in Hull Materials; Stresses in Hull Materials; Testing for Blister Resistance; Types of Blisters; Leaching of Substances from Hull Material; Long Term Effects of Water Up-Take. ~~Summary; Bibliography~~ Keywords

The much more detailed and highly technical report of ~~this work~~ is entitled "The Causes of Blistering in Boat Building Materials" also available from NTIS.

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NOTICE

FOREWARD

The problem of fiberglass gel coat blistering has plagued the boat business, both recreational and commercial, for the past 15 to 20 years, reaching significant importance within the past decade. Boat owners, especially those who had paid huge sums for highly competitive racing sailboats, were incensed when their $200,000 yacht developed a severe case of "boat pox." Other owners of less expensive craft - be they lobster boats or sport fishermen - were similarly horrified when they discovered what it cost to repair a blistered boat bottom. Boat owners pointed to their dealers who pointed to the boat manufacturers who pointed to their raw material suppliers. In the middle were the boat repair and service yards who were faced with repairing a problem that was entirely new to them, the cause of which they did not understand, and for which methods of repair ranged from slap dash to almost absurdly inefficient, impractical, and prohibitively expensive. The writer can testify to the above from first-hand experience in his New England repair yard.

Other considerations aside, however, the matter of structural integrity and, in the final analysis, the ultimate safety of the individual boat concerned many in this industry, and the U. S. Coast Guard in particular. Numerous well-intentioned studies had been undertaken by many factions in the boat building and material manufacturing industries, both in this country and especially in the United Kingdom, and the size of the bibliography of relevant printed reports is impressive. Many of these studies, however well intentioned, had been made by interested parties or focused on perhaps only one part of the problem. Many concerned persons felt that an in-depth and exhaustive study by a highly qualified yet completely impartial laboratory was necessary to establish once and for all the causes, prevention, and cure for the problem of osmotic blistering as the disease is now more accurately called. The American Boat Builders and Repairers Association (which is a national association of boat building, repair and service yards), taking the bull by the horns, made a small grant to the University of Rhode Island to undertake an initial study of the problems in 1984, hoping that other sectors would come forward to support this research. Unfortunately, and for reasons best known to them, such support was not forthcoming - and to tell the truth the suggestion was turned aside by some in distinctly antagonistic terms. By this time, however, the Coast Guard was very anxious to determine the true severity of the problem (or the lack of severity for that matter), and in 1985 approved a grant to the ABBRA in the amount of $60,600 to pursue an in-depth study of Phase I of the problem - the causes of blistering. The Association, in turn, contracted with the University of Rhode Island to do the research and to write a report on the findings of the research team.

This study was undertaken by Drs. Thomas Rockett and Vincent Rose of the U.R.I. Graduate School of Chemical Engineering, ably assisted by several graduate students, and was completed in the fall of 1986. The report itself, highly technical, is difficult if not impossible for the average layman to understand, but this highly-readable and condensed summary has been prepared for the interested public. We firmly believe that the $60,600 of taxpayers' money has been well spent, and that an enormous amount of hitherto unknown information has been discovered. Some theories have been discounted and others reinforced by scientific enquirey, and the net result is a solid base of information upon which boat builders, manufacturers, suppiiers and the basic synthetic materials industry can rely.

Phase II, the implications and techniques of blister repair and surface reconstruction, has been funded by a further Coast Guard grant of $78,500, and the necessary research is currently underway, also at the Univeristy of Rhode Island. A full report on this phase will be completed, hopefully, by the fall of 1987.

The American Boat Builders and Repairers Association would like to express its thanks to those in the Coast Guard in Washington who have been instrumental in helping us to obtain the necessary funding and to the members of the staff at the University of Rhode Island, especially Messrs. Rockett and Rose, who have so skillfully conducted this intricate research project to date.

Thomas Hale

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INTRODUCTION

Fiberglass reinforced polyester (FRP) composites, the structural material of many boats, are subject to a degradation phenomenon known as blistering. The surface blister is a bump that appears on the hull surface, usually under the water line. It grows because a pocket of acidic fluid developes within the hull. Blisters range in size from a few millimeters to several inches in diameter and normally occur near the gel coat-laminate interface but have been observed deeper in the hull. Blisters are very rarely seen in the gel coat material itself. Only in one case, where two layers of gel coat were used, were blisters observed to form at the interface within the gel coat.

Good statistical information on the occurrance and severity of blisters on boats does not exist. While we have seen over 100 cases of boat blisters, there is no statistically established correlation between boat age and blister onset, severity or depth into hull. The influence of the cycle of dry land storage to immersion is not known. Reports from warmer water locations suggest the problem is more severe than in northern areas. We have seen three cases in which the hull is severly delaminated and in which decomposed resin is found more than half way through the hull. These were boats which were more than 10 years old. Estimates of the number of boats showing blisters in given localities range from 1% to 90%. There is a belief among many marina personnel that the problem is more widespread now among newer boats than it was ten years ago. Again, this is unsubstantiated by reliable statistics but has been reported to us by many marina operators. Indeed, one manufacturer stated that prior to about 1980, they had never had a reported blister but since then, hundreds of complaints have been filed.

The cost of repair is significant to boat owners ranging from $10 to $200 per foot of boat and several boats have been declared unseaworthy because of structural damage associated with blistering. A solution to the problem must be found to restore consumer faith in glass-polyester boats. The University of Rhode Island and the American Boat Builders and Repairers Association undertook a research project on the blister problem which was sponsored by the United States Coast Guard. Through laboratory research, field observations and interviews, and a thorough review of past research work, the causes of blistering have been defined. The application of this knowledge will prevent many cases of blistering and direct future work toward minimizing the problem in new boats and permitting the successful repair of older boats. A technical report has been submitted to the Coast Guard which presents tabulated data and experimental details. This report, drawn on those findings, discusses the causes of blistering.

How Blisters Form

The first step in blister formation involves the movement of water into the gel coat material of a boat hull and then into the laminate material. All polymeric materials are subject to some degree of water permeation. Details of how the water moves through the laminate and the way the different materials and other factors effect the water movement will be discussed later. This water movement, by itself, is not harmful. It is a necessary step for blistering but this step alone is not sufficient to cause blistering without other contributing factors.

The second necessary feature of blister formation is the presence of small clusters of water soluble material (WSM) within the hull. These clusters are harmless and remain dormant until the permeating water molecules reach them and react with them to form tiny droplets of water and WSM locked into the laminate.

The minute droplet of solution is seperated from the surrounding water by the semi-permeable polymer membrane which consists of a gel coat and usually a thin layer of laminating resin. Water molecules can pass through this layer, but the WSM molecules cannot. Since the outside water and the solution are of different concentrations, water will permeate through the gel coat attempting to dilute the droplet of solution trapped in the laminate. This process is known as osmosis. During this process, more water enters the droplet causing it to expand and create a pressure on the surrounding hull material. It takes place whenever two solutions of different concentrations are seperated by a semi-permeable membrane. This increased pressure is referred to as osmotic pressure. Theoretically, the osmotic flow of water into the droplet should continue until the soultion has the same concentration as the water outside the hull. As water is drawn into the droplet, an outward force is exerted on the laminate and gel coat surrounding the growing solution. When the pressure exceeds the deformation point of the hull material it begins to flow or crack. This decreases the pressure and allows more space for water to be drawn into the solution. As the pressure grows, a blister forms on the surface.

The solution inside the blister is acidic because many of the WSM compounds react with water to form acids. Because the solution is under pressure, if the blister is punctured, the blister liquid will squirt out of the opening, sometimes at high velocity. Furthermore, if the boat is removed from the water, the hull will begin to dry causing water to permeate outward. Water will leave the blister solution as well and eventually the blister disappears. During this stage the WSM still remains and stays dormant until the boat is launched again at which time blister growth will begin again. This phenomena has been observed by many boat yard owners.

This brief look at blistering brings up many questions which were addressed during the study and which are also discussed in this report. Some of the questions which will be considered are the following:

- How do the WSM materials get into the hull?
- What controls water movement through the gel coat?
- How do different plastic materials affect water movement?
- What types of reactions take place between WSM and diffusing water molecules?
- What kinds of damage does blistering do to hull materials?
- Is there more than one type of blister?
- and finally, how can blisters be prevented?

The Hull Material

To fully understand blistering, it is necessary to have a working knowledge of the components of gel coats and fiber reinforced composites. In the currently used materials, which are the best polymer boat building materials ever developed, there are many components, each one of which is added to contribute an essential property to the final structure.

The unsaturated polyester resin liquid is made up of short chains of polyester molecules disolved in styrene. The styrene units can be considered as tiny ball bearings the same size as each link in the polyster chain. The chains are made up by joining three types of links together. The properties of the chain, such as strength, flexibility, and water resistance depend on the properties of each link, the number of each kind of link in each chain and the length of each chain. The links are glycols, phthallic acids and unsaturated acids. In altering the properties of a polyester, trade-offs must be made to optimize their use for boat building. A chain must contain a certain number of unsaturated units to give a strong polyester, but too many will yield a brittle material which will crack during use. A typical general purpose polyester liquid resin will have chains containing 16 links. Eight of these will be glycol units occupying every other link in the chain. Four of the links will be phthallic units (isophthalic, orthophthalic or terephthalic) and four will be unsaturated units. For each one of these chains there will be eight spherical units of styrene.

When the proper catalyst package or hardener is added, the unsaturated units in the chain form bonds with the styrene units or with short chains of polystrene. The polysterene chains join the polyester chains together at the unsaturated links hardening or curing the liquid into a three-dimensional network.

This setting reaction is called cross-linking or curing and produces heat which is extremely important in obtaining a complete cure since the heat envolved promotes further cross-linking.

The catalyst package for hardening the polymer contains several types of compounds. Only one of these compounds will become part of the polymer network. The others will remain in the free space between the chain units of the polymerized network. Table 1 lists the components of a polyester resin-glass composite. Also shown on the table are the constituents which do not become part of the network but reside in the free space. Those units which are water soluable can contribute to the blister problem under circumstances discussed below. From one to five percent of a completely cured resin can consist of water soluable material (WSM).

The second source of WSM units comes from the network formers as a result of incomplete cure of the resin. In Table 1, all the polyester groups should be bound into a three-dimensional network. Three things can convert network molecules into WSM units. First, incomplete cure, caused by poor mixing, low lay-up temperature, decomposed or aged peroxide, reaction of styrene with air, or improper catalyst package selection will mean that a certain fraction of the network formers will remain as WSM in the free space of the network. Second, in "cooking" the polyester, a certain fraction of material either does not react to form chains or forms short saturated chains that become WSM units. Thirdly, chemical reactions with water or acids can break down the network and convert parts of it to WSM units. All three of the above mechanisms can produce WSM in a resin. An example of this is the formation of free glycol which has been shown to cause blisters.

In making a gel coat material, a polyester resin is used for the base. To obtain the color and the hiding power desired, a pigment powder is blended into the resin. The resin is thickened to prevent run off by the addition of extremely fine silica powder. Certain clays can also be added to help the flow properties. Finally, extenders or fillers can be added to reduce the amount of resin needed in the gel coat and which in some cases add strength. During our study, four hull materials were analysed for the content of metal atoms. As shown in Table 2 the materials are chemically quite complex because of the variety of additives used to optimize properties.

An unanswered question which bears on WSM concentration concerns the curing mechanism of the hull material. We have assumed that during cure, all WSM units are trapped within the growing network. If during the lay-up, polymerization begins at the mold surface and moves outward, the WSM units could be pushed ahead of the moving gel boundary and concentrated at the free surface. These might be disolved in the next layer of resin and upset the distribution of WSM units locally. Evidence of this type of segregation has been discovered during this program. The full implications of this type of separation are not clearly understood at this time.

TABLE 1

Some Common Constituents in a Polyester Glass Composite Marine Material. Materials are classified as network formers (NET), water soluble units in the network (WSM) and stable additives (STAB).

1.	Polyester Groups	
	Orthophthalic acid or anhydride	(NET)
	Isophthalic acid or anhydride	(NET)
	Ethylene glycol	(NET)
	Propylene glycol	(NET)
	Neopentyl glycol	(NET)
	Maleic acid or anhydride (unsaturated)	(NET)
	Fumaric acid (unsaturated)	(NET)
	A phthalic acid, a glycol and a maleic are reacted to form the unsaturated polyester. The ratios can vary from 2p:1m:3g for a low reactive polyester to 1p:1m:2g to make a moderately reactive polyester to 1p:2m:3g for a highly reactive polyester. Ordinarily, a slight excess of glycol (1:1:2.1) is added to ensure termination of the chains by glycol units. Excess glycol or uncured components will contribute to WSM fraction.	(WSM)
2.	Cross-linking Agent or Vinyl Molecule	(NET)
	Styrene (40 to 50 weight percent) (unsaturated vinyl molecule) (Added styrene will yield a total ratio of 1p:1m:2g:4 styrene. The viscosity of the resin is largely controlled by the amount of styrene.)	
3.	Inhibitor: (0.1 - 0.5%) - added to increase shelf life.	
	Quinones	(WSM)
	Amines	(WSM)
4.	Ultraviolet Stabilizer (in gel coats 0.1 - 1%)	
	Benzophenones	(WSM)
	Hindered amines	(WSM)
5.	Colorants (in gel coat materials)	
	Inorganic pigments (1 - 5%)	(STAB)
	Organic pigments (1 - 5%)	(WSM)
	Carriers (phthalate plasticizers) (0 - 3%)	(WSM)
6.	Catalyst (initiators - added to react with unsaturated bonds and cause cross-linking and become part of network)	
	Azo-compounds	
	Methyl ethylketone peroxide (1 - 2%)	(NET)
	Benzoyl peroxide	(NET)
	Phthalate carriers	(WSM)
7.	Promoter (the true catalyst which activates the initiator)	
	Cobalt salts (octoates, napthenates, alsynates)	(WSM)
	Anilines (dimethyl)	(WSM)
	Mineral spirit carriers (toluene)	(WSM)

TABLE 1 (continued)

8.	Reinforcement	
	(Mats, woven fabrics, chopped fibers)	
	Glass surface ions leached through long-term acid exposure	(WSM)
	Fiber glass - Silicate network with calcium, sodium	(STAB)
	magnesium and aluminum	(WSM)
	Aramid Fibers - Carbon Fibers	(STAB)
9.	Coupling Agents (bond formers between the polymer and the glass)	
	Various silane compounds	(STAB)
	Titanates, Mordants (chromium compounds)	(STAB)
	Reaction products from long-term acid exposure	(WSM)
10.	Sizing (lubricants and handling agents added during fiber glass manufacture)	
	Starches and emulsions. Most are burned off before composite manufacture.	(WSM)
11.	Binders (added to hold mats & filaments together)	
	Polyvinyl acetate emulsions	(WSM)
	Polyester powder	(STAB)
12.	Thixotropes (added to prevent runoff of resin)	
	Utrafine SiO_2	(STAB)
	Clays	(STAB)
	Acid leachate from clays	(WSM)
13.	Fillers (added to reduce cost)	
	Clay	(STAB)
	Talc	(STAB)
	Limestone	(STAB)
	Ions leached from fillers	(WSM)
14.	Waxes (added to prevent air inhibition and as mold release agents)	(STAB)
	cause localized low strength zones.	
15.	Wetting Agents (added to lower interfacial energy and enhance resin wetting of glass)	
	Oleates, stearates, emulsifiers, surfactant	(WSM)
16.	Flame Retardants	
	Halogenated compounds	(WSM)
	Aluminum hydrates	(STAB)
17.	Impurities (can enter at any stage in which new materials are added)	
	Water, Benzene, Aldehydes, Ketones, etc.	(WSM)
	Dirt, dust	

Table 2. Qualitative X-Ray Fluorescent Analysis of Typical Polyester resins and Gel Coat Materials

	Isophthalic (Neopentyl Glycol)		Orthophthalic (Neopentyl Glycol)	Orthophthalic (Propylene Glycol)	Vinyl	Possible
Element	Gel Coat A	Gel Coat B	Gel Coat	Resin	Gel Coat	Sources
A1	Moderate	Moderate	Moderate	None	Moderate	Fillers (clays) or Flame Retardants
As	Trace	Trace	Trace	None	None	Fillers (clays)
Br	Trace	Trace	None	None	None	Fillers (clays)
Ca	High	Moderate	High	Low	None	Fillers (CaCO3 or clays)
Co	Low	Low	Low	High	None	Promoter
Cu	Low	Low	Low	Trace	None	Promoter
Fe	Moderate	High	Moderate	Low	High	Fillers (clays)
K	Low	None	Low	None	Moderate	Fillers (clays)
Mg	Moderate	High	High	None	Moderate	Fillers (MgCO3 or clays)
Mn	Low	None	Low	None	Low	Fillers (clays)
Rb	Trace	Trace	None	None	None	Fillers (clays)
S	Moderate	Low	Low	None	Low	Resin
Si	High	High	High	High	High	Thixotrope and Clays
Sr	Low	Low	Low	None	None	Fillers (clays)
Ti	High	High	High	Low	High	Pigment

A certain level of WSM is essential to a well designed resin. Their presence does not result in a composite of low blister resistance. However, if they are concentrated beyond normal limits or if they are concentrated at a given zone, blistering will result.

Resin manufacturers continue to develope these polyester materials to improve the properties. Table 1 gives some idea of resin complexity. Changes in formulation to improve one property could decrease another property. Boat builders must test all incoming materials for blister resistance. A simple 100 hour boil test will warn of potential problems. This test can be performed by placing a 4"x4" test laminate in boiling water for 100 hours. New materials must be certified by the boat builder and familiar materials must be tested to guarantee the quality is maintained from batch to batch.

Manufacturing Processes

Boat hulls are usually made from the outside-in by applying the gel coat to a waxed mold and then adding the layers of glass reinforcement and polyester to complete the hull. The gel coat, the pigmented and filled polyester, is used to hide the underlying glass composite structure, to color the hull, to produce a flexible surface which acts as a shock absorber and to help keep water from diffusing into the composite. It is usually sprayed onto the mold to a thickness of 20 mil (0.020") which as curing takes place will shrink to a thickness of 14 to 18 mils. The gel coat can be cured by mixing the catalyst and spraying or rolling this "hot" mix on to the mold within the 10 to 20 minutes available until setting. It can also be applied by co-spraying the catalyst and resin using a variety of commercially available spray guns. In both cases, good mixing is critical. A clogged or partially clogged nozzle will give an under cured resin which will have little blister resistance because constituents which should be in the network remain unpolymerized as WSM. Also, the peroxide catalysts have limited shelf life. They should be stored cold, kept well sealed, used at temperatures above 60^{o}F, and never used beyond the manufacturers expiration date. The gel coat should be applied as one continuous layer. If it is put on in several layers, with a cure cycle between layers, blistering can take place at these interfaces. The gel coat should be applied as thickly as possible since added mass increases the cross-link heating which aids curing. A thicker gel coat also acts as a more effective water barrier. In practice, a 35 mil, wet, gel coat is about the maximum which can be achieved without run-off from the mold.

An air inhibited layer produced at this point in manufacture can lead to blistering. Styrene, the cross-linking units, can react with air to form benzaldehydes which are water soluble. If the styrene is consumed near the surface by reaction with air, the surface polyester will not cross-link and will remain tacky even after the bulk has completely cured. The surface layer will be enriched in WSM and blistering will be promoted. Several things have been done in our laboratory to minimize this problem. Some are impractical in manufacture. They are listed below:

1. A thicker coating gives a hotter, faster set which reduces the time the styrene can react with air. At least 30 mils, wet, should be applied.
2. The air inhibited layer can be stripped off with acetone. However, if this is not done with care, it could exaccerbate the problem by producing localized areas of concentrated WSM.
3. A wax can be added to the resin which floats to the surface during cure and keeps air out but this also introduces problems. The wax must be removed before continuation of lay-up.
4. A wax paper barrier can be applied to the surface after the lay-up to keep air out during curing. However this is difficult because the pressure of applying the wax paper to the wet gel coat destroys its uniform thickness.
5. A water soluble barrier layer, such as P.V.A., which is applied and washed off after the cure, has been tried. While this technique looks promising, further tests must be performed to prove it's effectiveness. Thorough removal is critical since the P.V.A. left behind will be disolved in the next layer of resin and by becoming a source of WSM will cause blistering.
6. The gel coat can be heated in the spray gun or on the mold with a moving bank of lamps or other heat source. This will help reduce the air inhibited layer by increasing both the rate and degree of cure.

Removal of the air inhibited layer by sanding produced severe blisters because the sticky material was not removed but was repacked into the surface. In practice, the best way to avoid an air inhibited layer under the gel coat is to use a thick layer, heat it, and continue lay-up as soon as possible. It will be obvious to the reader that many of the suggestions made here with regard to gel coats are also applicable to resin lay-up interfaces.

Once the gel coat has become tacky to the touch, laminating resin is sprayed onto the gel coat and a reinforcing mat is applied with serrated rollers. This is done to squeeze out entrapped air, to obtain thorough wetting of the glass by the resin and to keep high glass to resin ratio. Some entrapped air bubbles are inevitable and do not themselves cause blistering. Densification should be as complete as possible because air bubbles greatly reduce composite strength.

For a variety of reasons associated with matching coefficients of expansion, moduli of elasticity and swelling stresses associated with water pickup, it is accepted practice to put a resin rich layer between the gel coat and the first structural layer. A veil mat or light chopped glass layer is placed between the gel coat and the laminate.

The selection of glass in this layer and in the underlying laminate must be chosen with a binder which is not water soluble. Water soluble binders cause blistering because they are WSM. Some of the roving used in chopper guns is emulsion bound and burn-out tests show one to five weight percent of binder can be removed from chopper glass. This concentration of WSM under the gel could result in blisters.

There have been some major changes in manufacturing processes since the early fifties. Some of these changes were the result of design changes, some the result of material changes, and some the result of regulatory changes. The use of spray-gun equipment increased drastically in the 1970's. Catalyst compositions were altered by the Department of Transportation Shipping regulations in the late 1970's. These regulations reduced the percent of active oxygen in the MEKP catalyst from 11% to 9%. OSHA regulations issued in the early 1980's may affect resin compositions. Oil prices also could alter the source of resin and the percent of filters used. If statistical information on blister frequency were available, these data could be correlated with such changes to isolate cause and effect relationships.

Water Diffusion in Hull Materials

Once a fiber-glass boat is put in water, water diffusion through the gel coat begins. All polymers (plastics) exhibit some degree of water diffusion. Diffusion is the site to site jumping of single water molecules through the gel coat. The water molecule enters the free space between the chains in the polymer network and jumps to the next open site. This differs in many important ways from the flow of water through pin holes.

Molecular diffusion controls the permeation rate or rate of water movement through the hull. Water diffusion through polymers is related to the following factors:

1. The ease with which the water molecule can jump from one site to the next. This is expressed by the diffusion coefficient and is related to the strength of the forces acting on the water molecule by the atoms in the polymer network.
2. The difference in water concentration at any two points in the hull. As the concentration difference increases, water moves faster. When the concentration at the two points becomes the same, water movement stops.
3. The amount of water which the polymer can hold which is known as the saturation level. This controls the concentration difference

and is different for each polymer. It is essentially the number of sites in the network available for occupation by a water molecule. The degree of cross-linking can affect this greatly.

4. The temperature of the polymer. The rate of water movement increases with temperature so that an 18°F temperature increase will cause water to move twice as fast.

5. The amount of filler or glass in a polymer reduces the sites available for water and reduces water transport.

This movement of water through the hull structure can be expressed mathematically by a series of laws known as Fick's laws. Using these equations, a computer model was constructed during this study. The model was used to predict the water concentration throughout the hull structure at any given time for a range of different polyester materials.

The major finding from these results indicate that if the resin composition changes at an interface, a discontinuity in water concentration will result. This discontinuity has some implications to blister formation because it affects the stress at the interface. In general, the rate at which water moves through the gel coat in a composite which will blister determines the time at which blistering begins. Water diffusion does not cause blistering but is is an important step in the sequence of events which lead to blistering.

Stresses in Hull Materials

Corrosion and degradation processes are greatly affected by localized stress. This is true for all materials and is particularly true of polymers. There are four sources of localized stress in a boat hull all of which can influence blister formation and growth. The four are:

1. Stresses are produced by polymer shrinkage during curing. After the gel coats are cured on a mold, the resin is applied. It bonds to the gel coat before it cures. The resin near the gel coat interface goes into tension as the resin away from the interface cures and shrinks.

2. Stresses are produced by swelling of the resin due to water diffusion. The amount of water present causes swelling of the polymer. Our measurements, and literature values show the resin can swell as much as 10 percent by volume and this is greatly affected by the degree of cross linking. Stresses are generated by differential swelling. If the entire hull swells uniformly, no differential stress will result. However, if one layer swells and the adjacent layer does not, the adjacent layer will be pulled apart (put in tension) by the swelled layer. The level of differential stress generated

will be determined by the water gradient and discontinuities in the gradient and not by the absolute amount of water present.

Figure 1 shows the relationship between water concentration and stress development. Note that the maximum tensile stress will develope under the surface and ahead of the diffusing water. If the tensile strength of the polymer is exceeded at the maximum tensile stress position, disk cracking will take place. Figure 2 shows such disk cracks formed under the surface of clear resin.

The stress is transient. The maximum tension will move inward and decrease in magnitude as water diffuses. If the resin has high strength, that is, it is well cured, highly cross-linked, and reinforced with glass, it can survive the passing stress field and not crack. If a disk crack forms, it constitutes a vacuum. Any local WSM units will be drawn toward the crack to increase the pressure. This is a mechanism for concentration of WSM units in the vicinity of the crack. Figure 3 shows a localized concentration of cobalt from the resin promoter concentrated in a disk crack. Our conclusion is that stress cracks can create blister centers.

The stress build-up can have an effect on water transport and lead to concentration gradients which would not be predicted by Fick's Law. As the resin network goes into tension, the free sites are opened and water advances faster than anticipated. This can lead to a diffusion profile with a sudden drop. A water front moves through the polymer. Behind it the polymer is close to saturated; in front of it the polymer is dry. To establish the shape of the water profile, water concentration measurements at different depths at given times must be measured.

3. Stresses are produced during boat use. Peak stress is produced by wave action, rigging stresses, impact stresses and bouyancy stress.

4. Internal cracks produce stress concentration sites at the crack tips which can lead to further cracking or accelerated chemical attack. Strictly speaking, the crack does not produce a new stress but intensifies one of the above three stresses. Cracks can magnify a stress by hundreds of times.

Two or more of the above four types of stress can interact at a particular point in time and space. For example, if a modest shrinkage stress combines with a small water swelling stress and at the same time, severe wave impact flexes the hull, localized disk cracking can take place. Furthermore, the reaction of the polyester resin to the stresses applied is dependent on the flexibility and toughness, i.e. resistance to cracking, of the resin. If the resin is brittle cracking will occur. A flexible resin can deform under peak stress

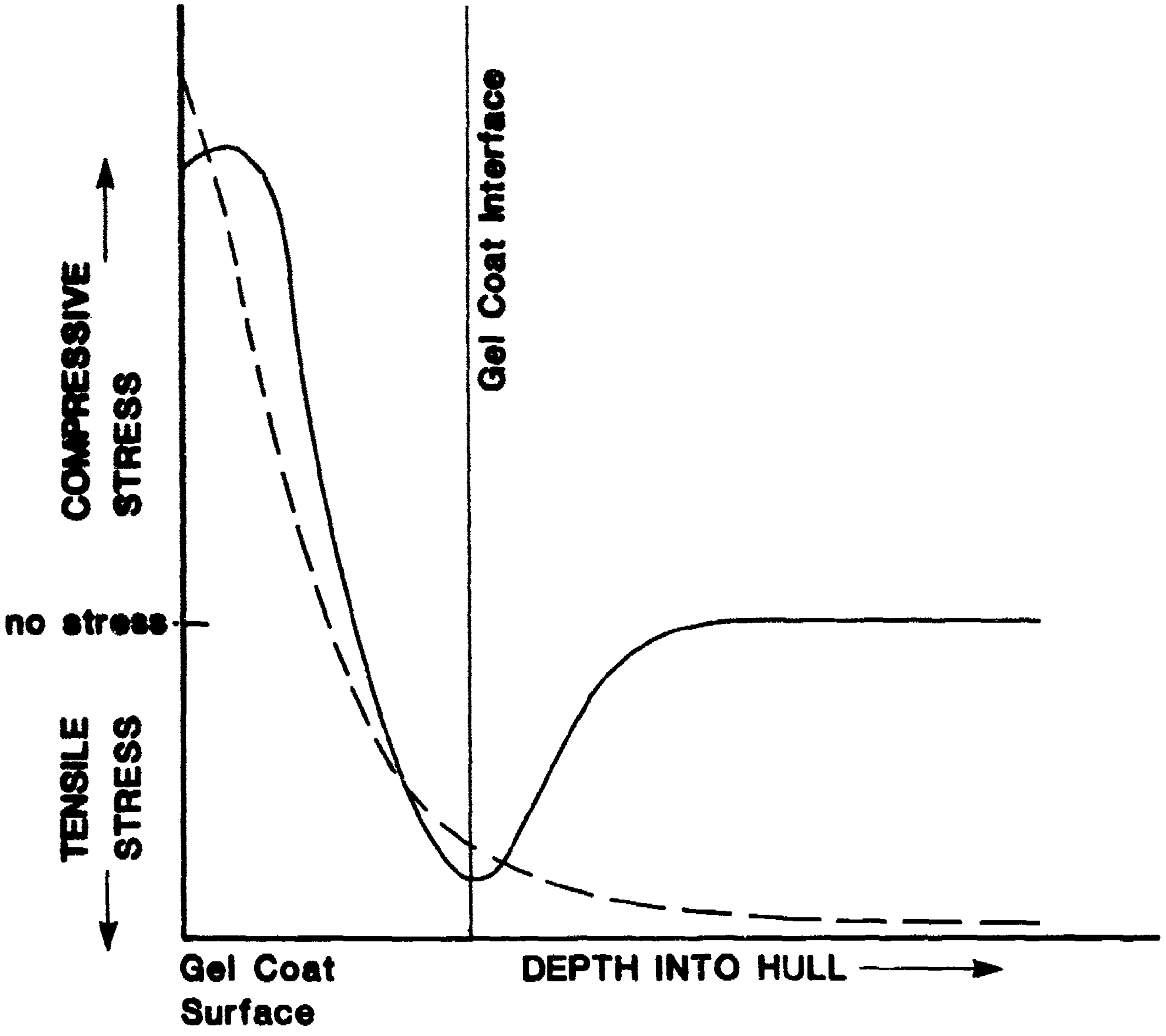

Figure 1. Sketch of a laminate cross-section.

The amount of water absorbed by the polymer is plotted with the dashed line. The absorbed water generates swelling stresses which are indicated by the solid line.

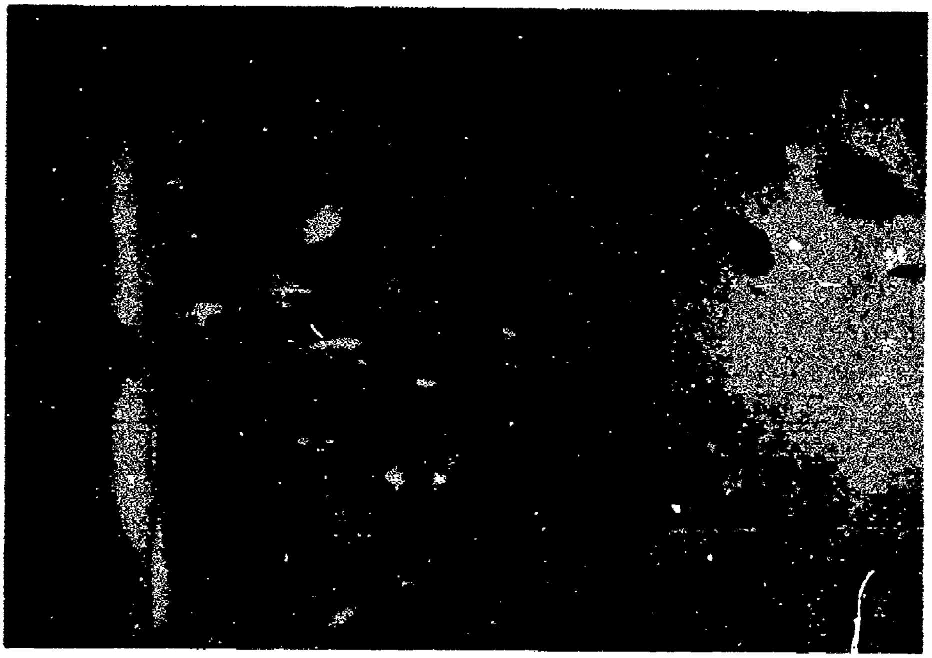

Figure 2. Photomicrograph of disk cracks (stress cracks) in a polyester resin. They are circular internal cracks which are about 1 mil in diameter.

Figure 3. Micrograph of a disk crack surrounded by a purple halo which is caused by a high cobalt concentration. The cobalt from the promoter salts was drawn into the vacuum associated with newly opened disk cracks.

loads without cracking. Resin flexibility depends on the type and number of links in the polyester chain and, very importantly, on the number of cross-links between the chains.

Testing for Blister Resistance

In order to decide which materials are best for hull manufacture and which parameters reduce blister susceptibility, 168 sample laminates were made and tested during this study.

Gel coated test laminates were made by hand lay-up techniques, using both brushed and sprayed resins, following standard manufacturing techniques. The typical panel, made on a waxed glass mold, was 2'x2'x1/4". Table 3 lists the materials used. Polymerization was initiated using methyl ethyl ketone peroxide according to manufacturer's instructions. The fiber glass reinforcement was three layers of woven roving. Various types of resin rich construction were used between the gel coat and the roving. This included one or two layers or combination of layers of 3/4 oz. veil, 1-1/2 oz. mat and approximately 20% by weight chopped gun roving. The panels were made and post cured to constant Barcol hardness values at the same temperatures. Most were made and post-cured at 75^{o}F but a series were made and post-cured at 50, 70, 90, 100^{o}F to test the effects of manufacturing temperature.

Samples were tested for blister resistance by immersion in a 65^{o}C (149^{o}F) constant temperature water bath. Figure 4 shows the acrylic sample holders which were designed during this project and used for one sided exposure. Samples were examined on a routine basis for blistering. The longest exposure time was 24 months. Blister initiation time, the time at which blisters are first observed, and blister severity (number and size of blister per cm^{2}) were measured. Representative samples were cross-sectioned for polarized light microscopic examination and measurement of gel coat thickness. Two sets of each laminate were fabricated and tested.

In general, the test panels fall into five categories:

1. A series of NPG-isophthalic gel coated TMPD-isophthalic laminates, in which gel coats were obtained from three different suppliers.

2. A series using NPG-orthophthalic, NPG-isophthalic and vinyl gel coats and PG-orthophthalic and NPG/EG isophthalic laminating resins.

3. A series of NPG-isophthalic gel coated, PG-orthophthalic laminates made up and post-cured at 50, 75, 90 and 100^{o}F.

4. A series of NPG-isophthalic gel coated, PG-orthophthalic laminates in which various types of glass were used in the resin rich layer beneath the gel coat, and

TABLE 3

Chemical composition of polyester gel coat and laminating resins.
(Stars designate presence of constituent material.)

GEL COATS

MATERIAL SUPPLIER	IPA (NPG)	OPA (NPG)	VINYL
1	*		
2	*		
3		*	
4	*		
5			*
6	*		
7	*		
8	*		
9	*		

LAMINATING RESINS

MATERIAL SUPPLIER	IPA	OPA	NPG	EG	PG	TMPD
1	*		*	*		
2		*		*		
3		*			*	
4	*					*
5		*			*	

IPA - ISOPHTHALIC ACID
OPA - ORTHOPHTHALIC ACID
NPG - NEOPENTYL GLYCOL
EG - ETHYLENE GLYCOL
PG - PROPYLENE GLYCOL
VINYL - URETHANE BASED POLYESTER RESIN
TMPD - 2, 2, 4 - TRIMETHYL - 1, 3 PENTANE DIOL

5. A series of NPG-orthophthalic gel coated, PG-orthophthalic laminates in which the effect of air inhibition of the gel coat was tested.

Figure 5 presents the results for blister initiation time on various samples. Other factors aside, the initiation time is a function of gel coat thickness as discussed in the section on water permeation. Comparisons of different laminates for blister initiation are meaningless unless gel coat thickness is either constant or the initiation time is corrected for thickness variations. A dry 30 mil gel coat will not show blistering for at least twice the time that a 15 mil gel coated laminate begins to blister.

Figure 5 shows that blister initiation time is also a function of both the laminating resin and the gel coat formulation. In rating the laminating resins for initiation time, orthophthalic resin was best in all cases. For the gel coat, the rating depended on the laminating resin. The NPG-orthophthalic gel coat was better than NPG-isophthalic which was better than vinyl when used with PG-orthophthalic laminating resins. When these same gel coats are used with isophthalic laminating resins the order becomes NPG-isophthalic was best, vinyl was intermediate and NPG-orthophthalic blistered most quickly. It appears from the birefringence, which is an optical effect caused by stress and is observed using a polarized microscope, that residual stresses created during lay-up and stresses produced by water diffusion related swelling account for some of these differences.

The severity of blistering, as measured by the density and size of the blisters, was a function of the laminating resin used if all other factors are kept constant. The orthophthalic resin resulted in fewer but larger blisters while isophthalic resin produced more but smaller blisters. In both cases, the total area affected was about the same. However, when vinyl gel coats were used, orthophthalic and isophthalic laminates produced small blisters, in both cases, and approximately the same number of blisters per square centimeter.

The blister initiation time was approximately the same for similar gel coat materials regardless of the supplier. However, the severity of blistering varied greatly among similar gel coats from different suppliers. One reason for this could be the difference in filler and extender contents in different gel coats made from the same base resin. While other gel coated orthophthalic laminate panels showed the best blister resistance, there is reason to believe that prolonged exposure to water may deteriorate the strength of these laminates faster than isophthalic laminates. Our studies on this aspect are continuing.

The series of experiments made to test the effects of laminating and post cure temperature showed that a lay-up temperature between 50 and 90°F did not have a major influence on blister resistance. These NPG-isophthalic gel coated orthophthalic laminates did show an effect of temperature at 100°F. The high temperature post cured laminates showed a high density of blisters sooner than the 90°F laminate and the blisters were very small (less than 0.4 mm^2 surface area). No significant difference could be found in the blister

Figure 4. Acrylic test tank designed for single-sided exposure of the laminates with the 65°C distilled water.

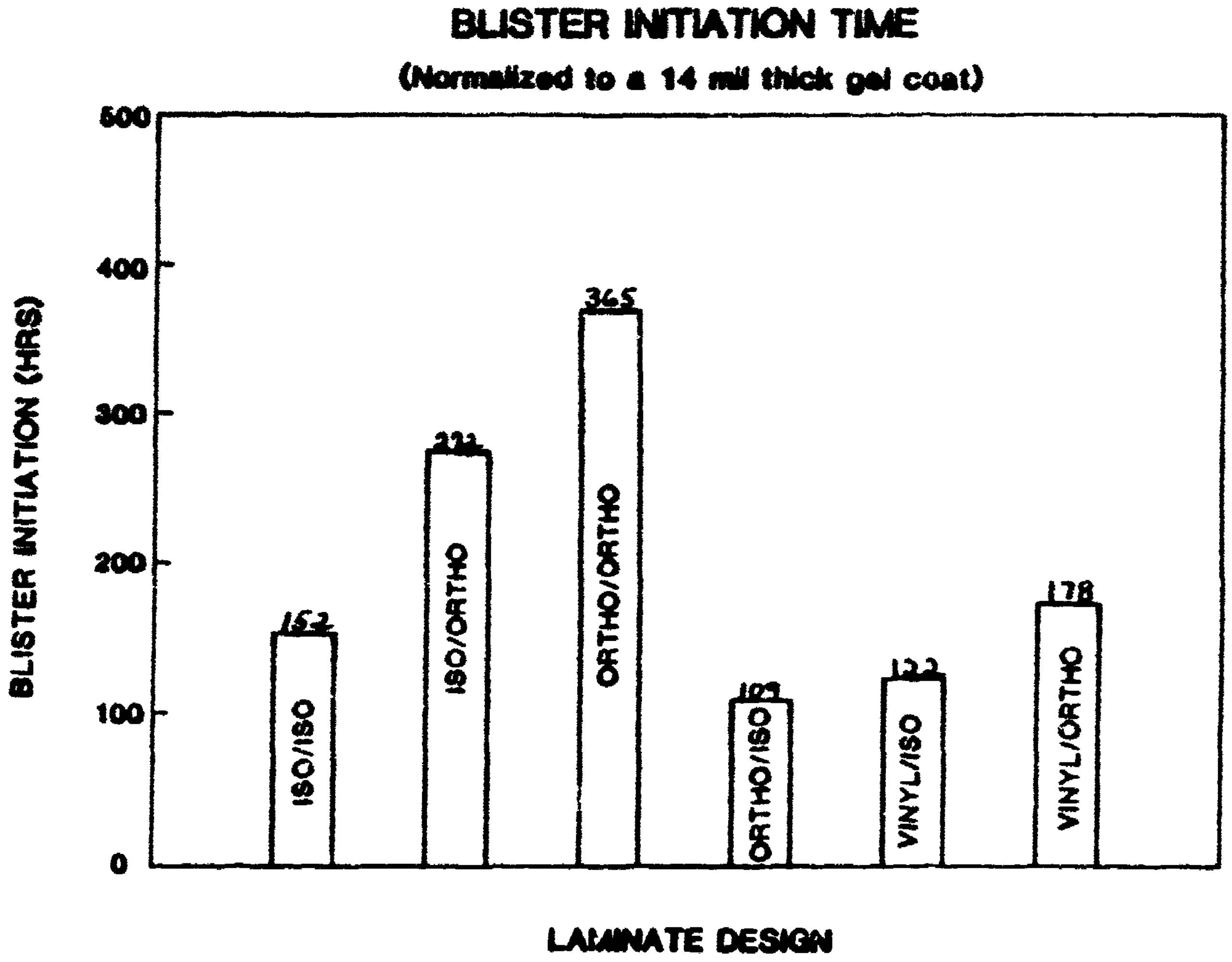

Figure 5. Blister initiation versus resin combination at 65°C (149°F)

All gel coated thicknesses have been normalized to 14 mils.

initiation time for the 50, 60, 70 or 90^{o}F laminates. With these samples, as well as all the other samples, there was considerable variation between samples. In addition, the blister initiation time was not an indicator of blister severity. Samples which blistered early, may or may not develope a severe case of blisters.

As reported previously glass binders can play a significant role in promoting blister severity. Samples made with a chopped gun roving, resin rich backup layer showed early and severe blistering. The gun roving was found to contain a binder which was applied as an emulsion. The amount depended on the supplier. Samples made with veil mats showed intermediate blistering while a 1-1/2 oz. of powder bound mat used in the resin rich backup layer showed superior blister resistance. Other studies are continuing using a variety of reinforcement glasses.

Preliminary results on the importance of an air inhibition layer at the gel coat-laminate interface show that exposure of the gel coat to air severly decreases blister resistance. It appears that the air inhibited layer dissolves in the laminating resin and promotes blistering. The nature of this air inhibited material and its role as a WSM is discussed above in the section on manufacturing.

Types of Blisters

Our findings indicate that there are at least two and perhaps three types of blisters.

The first type we call WSM concentration blisters. Using red dye, tiny colored grains of pressed sorbitol, a WSM, were placed into the laminate under the gel coat during construction. The exact location of the sorbitol could easily be seen when the panels were viewed from the glass/resin side. These panels were placed in the water test tank and in less than 24 hours blisters began to form at the exact location of the red particles. The remainder of the panel was unblistered.

This experiment confirmed the long held belief that pockets of concentrated WSM will cause blistering. The speed at which they formed was unexpected. This corresponds to blister formation in a month in water at 60^{o}F. To have WSM concentration blisters, a local zone of WSM must be introduced into the gel coat or laminate at some time during manufacture. Poor attention to good housekeeping practices during lay-up can result in this type of blister. Our microscopic examinations have shown debris and wood particles at gel coat interfaces that have caused blisters. Excess catalyst, accidently sprayed onto or placed in the laminate can also create such blisters. A clogged spray nozzle which does not deliver catalyst to an area or delivers an improper amount and leaves a zone of uncured resin will also act as WSM and result in a zone of blistering. Improper triggering of a spray gun also can lead to undercured resin or zones that are over saturated with catalyst. A large zone of air inhibited resin is a concentrated zone of WSM and will result in blistering. A thick coating of water soluble binder on glass reinforcement is a WSM concentration and as soon as water soluble reaches it osmotic pressure will begin to grow. It is possible that a particular resin could contain inordinate amounts of WSM because of an additive or water soluble filler. Boat builders may recognize other sources of WSM that are not listed here. The size of blisters will be related to the size of the WSM concentration sites. The extent of blistering on a hull will depend on the number of WSM sites and can vary from one to many. The time that the blister begins to form will depend on the depth of the WSM in the laminate, the permeation rate of water through the gel coat and the length of time continuous immersion of the hull. In severe cases, WSM concentration blisters can form above the water line. In a humid environment the hull will pick up water from the air. If the WSM is close to the surface, it can build a high enough osmotic pressure to draw in water and cause blisters from the humidity in the air.

There is a second type of blister to which a well made hull with no built in WSM pockets is susceptible. We call these stress induced blisters. In these blisters the WSM concentration is formed during the immersion of the boat. The mechanism for formation is the following:

1. When gel coat material is applied to the mold the surface away from the mold is cured in the presence of air which produces an air inhibited layer containing water soluble benzaldehydes.

2. When the laminating resin is applied, this water soluble material is dissolved in the first layer of the laminate.

3. As the laminating resin cures it bonds to the solid gel coat and then shrinks on curing producing a tensile stress in the laminate near the gel coat interface.

4. Upon immersion of a polyester laminate, water begins to diffuse into the polymer network.

5. This water absorption produces a swelling of the gel coat.

6. As the swollen layer tries to expand it produces tension in the underlying dry layer to which it is bonded.

7. This tensile field which lies ahead of the advancing water front produces stress or disk cracks in weak or brittle resin. The stress field is maximized by combination with the polymerization stressed zone.

8. When the disk cracks open, they create a localized vacuum into which adjacent water soluble molecules can diffuse. The water soluble material produced by air inhibition is already present in this zone.

9. Diffusing water molecules reach the cracked zone and interact with the now concentrated water soluble material forming a concentrated solution.

10. At this point, the osmotic process begins. Water is drawn into the zone producing osmotic pressure which builds until the creep stress of the polymer is exceeded and a bubble appears in the gel coat. From this process, stress induced blisters form just below the gel coat-laminate interface and stress plays a role in their nucleation. Our microscopic examination of many samples obtained from blistered boats show this to be the most common site for blisters to be located. Figures 6 and 7 show two cross-sections through blisters. One picture was taken using an optical microscope and the other was made with the scanning electron microscope. Both show the blister is located just under the gel coat and in the laminate a zone of disk cracks is shown at the blister depth.

Finally, if a boat is made so that no WSM concentration blisters form and the hull material resists cracking during water diffusion so that no stress induced blisters form will the boat last forever without blistering? Perhaps not. There may be a third type of blister, known as long term blisters, that could form and these are discussed below.

Leaching of Substances from Hull Material

There is a process that prevents blistering which must now be discussed. Some WSM units are absorbed on to the chains inside the polymer network when water begins to diffuse inward. Table 1 lists many of the possibilities. These are not harmful unless they are concentrated.

A phenomenon known as leaching or extraction of WSM from the gel coat and laminate during water immersion plays an important role in blistering. When one makes coffee or tea he makes use of the leaching process. The hot water extracts from the bean or leaf the soluble flavor-producing chemicals, leaving behind the spent grounds or leaves. By the same process water can extract certain WSM from the hull.

WSM units are held onto the polymer chains by weak forces. These forces can be eliminated by water molecules. When water diffuses into the hull, it dislodges WSM from the polymer chains, surrounds it with water and aids in the outward movement of the WSM. Figure 8 shows the weight change of two composite samples made in this study. The initial weight gain of the samples is due to water molecules moving into the polyester network. At 600 hours of immersion time, the sample begins to lose weight. This weight loss is caused by leaching and extraction of WSM from the resin. After a very long time,

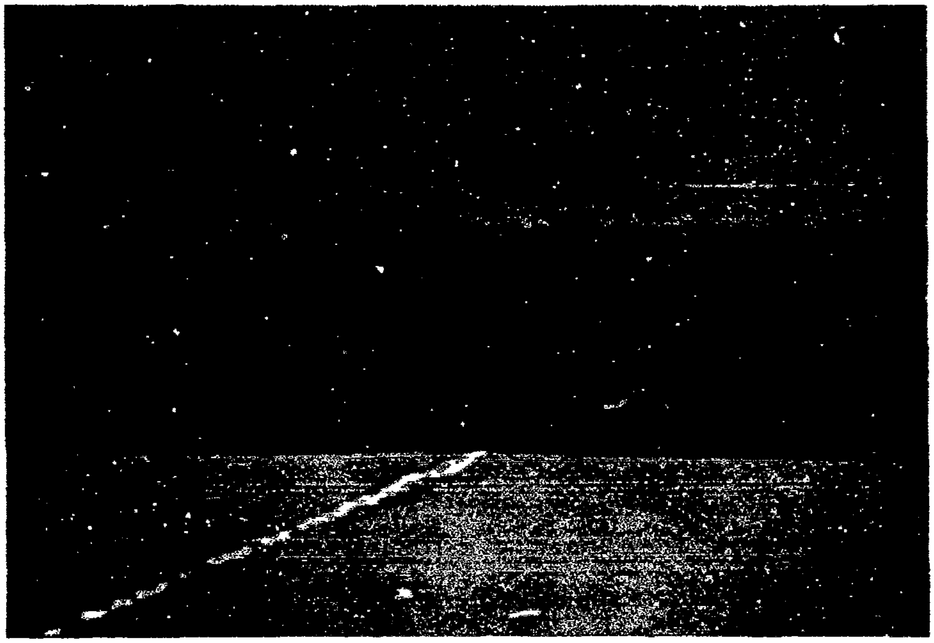

Figure 6. Cross-section of blister showing crack growth and deterioration of polymer at the crack tip and the surface exposed to the blister solution.

Length of blister is one inch.

Figure 7. Scanning electron micrograph of a blister under a gel coat showing the interaction of the growing blister with stress cracks. The white phase is glass fiber. The circules are air bubbles. Gray phase is resin. Black regions are the blister and the stress cracks. Gel coat is seen above the blister.

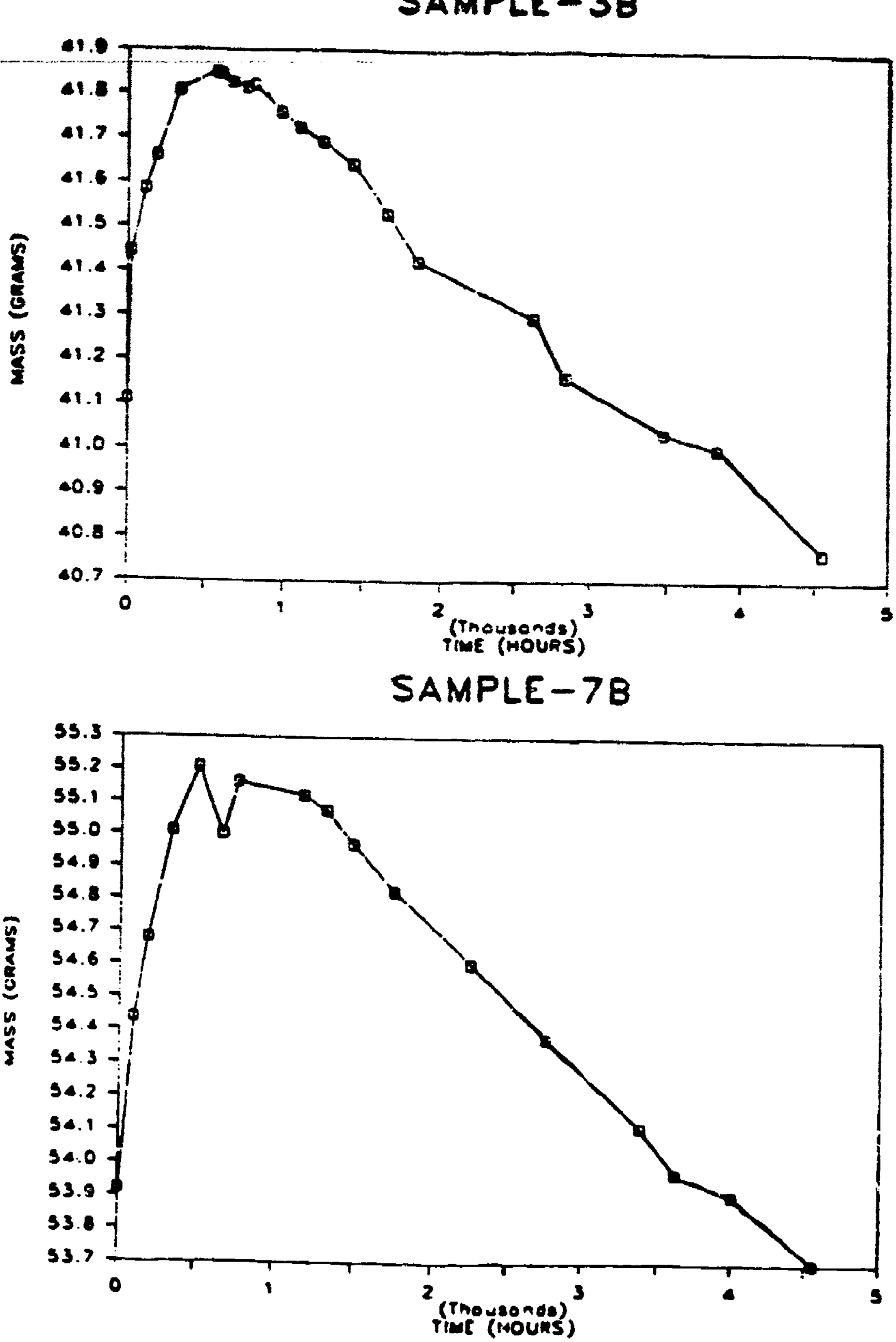

Figure 8. Observed net weight changes for typical polyester composites. Samples were exposed to 65^0C distilled water on all surfaces.

more than 4000 hours, parts of the network and some of the glass can also be attacked and leached out of the hull. The point at which weight loss overcomes water pick-up corresponds to about one year of continuous immersion in warm waters (76°F) and about three years of continuous immersion in cold water at a temperature of 55°F.

Leaching can cause crazing or cracking of gel coat materials. As leaching takes place, polyesters shrink in size. As the surface shrinks, small cracks form. As leaching continues, the cracks spread and intersect to form a crazing pattern. Currently available gel coats are remarkably free of excessive leaching. Of the eight gel coats examined in this study, only one showed severe crazing and this was an experimental material.

Excessive leaching will prevent blistering. In order to form blisters, the WSM must remain trapped inside the laminate. The inward movement of water, coupled with the inability of WSM to move outward, are required to generate osmotic pressure which causes blister growth. If WSM can move out as water moves in, blisters can not form. Many of the older polyester boats which did not blister, but showed crazing, probably were made of highly leachable polyesters. The group at the University of Rhode Island has developed a method for increasing the leachability of WSM from composites and thereby preventing blister formation. What is not known, at this point, is the effect of the porous gel coat on the long term strength properties of the polyester. This is a subject on which research is continuing.

Long Term Effects of Water Up-Take

We have seen that diffusing water can form internal solutions with WSM to form blisters and that diffusing water can leach WSM from the polyester. There are some additional types of water/polymer interactions that can influence the long term strength of hull materials and possibly lead to a third type of blistering. Concentration of WSM creates the first type of blister. Stress induced blistering is the second type. The third type, long term blistering, is proposed but has not been established in the laboratory. Long term blisters would form only after the hull material is saturated with water. Field observations suggest this type of blister may form. Work is continuing to prove or disprove their existence.

In addition to the interactions of WSM with diffusing water molecules discussed above, water molecules also can react with certain WSM to form acid solutions. After very long immersion times, small zones in the polymer network contain acid solution. While the acid may not be concentrated enough to form a blister at this stage, it can attack the polymer chains and break off links which are then dissolved in the liquid. This reaction is known as ester hydrolysis. It is self perpetuating because the addition of the broken link to the solution creates additional acid which leads to more attack. Furthermore, as this solution becomes concentrated by dissolving more links it can generate osmotic pressure. Hence, this slow acid attack converts some of the polymer network into WSM. The process is slow but it could yield long term or the third type of blisters.

There are certain types of fire retardant components used in some resins which make up links in the polyester. A brominated phthalic group is one such material. These units react with water to form stronger acids than phthalic acid. This acid can attack the polyester at a greater rate than normal and cause long-term blistering.

The acid solution which forms inside the first and second type of blisters can also attack the polymer around the blisters by ester hydrolysis. This results in polymer network attack. Links that are removed from the network become WSM units and continue the growth of the blister. The exact extent to which blister solution corrodes the surrounding polymer is not known and more work is required on this problem.

Summary

Listed below are the major findings of the American Boat Builders and Repairers Association/University of Rhode Island research project. The reader is urged to consider the implications only after a thoughful reading of the text.

1. Currently used glass reinforced polyester laminates are excellent materials for boat building, but under some circumstances, can exhibit blisters.

2. All resins contain some water soluble material (WSM). Only if that material is concentrated at a point in the hull will it cause blistering.

3. All blisters are caused by water diffusing into the hull and reacting with water soluble material to form a droplet of solution which, because of osmotic pressure, grows in volume and creates a force which results in a blister.

4. Three types of blisters are discussed. Water soluble material concentration blisters are formed from clusters of materials present in the hull when the boat is built. Stress induced blisters form because water soluble material is concentrated by water diffusion and stresses. Long term blisters form because of ester hydrolysis of the polyester molecules.

5. Other factors being equal, gel coat thickness determines when blisters will begin to form.

6. Laminate lay-up and post-cure temperatures did not have a major effect on initiation time or severity for temperatures between 50°F and 90°F. Higher temperature post cure should improve laminate stability. The degree of cross-linking is a critical parameter in determining the properties of a resin.

7. Design of the resin-rich region between the gel coat and laminate is important in minimizing blisters.

8. Control of air inhibition during lay-up can improve blister resistance.

9. Microscopic examination of blisters indicated presence of saw-dust, disk cracks, promoter and internal stresses in the blister region. Without such examination it is impossible to pin point the exact cause of blistering in a particular boat.

10. Leaching of material from gel coats will cause surface crazing of the material.

11. The blister initiation time and the severity of the blisters formed during this study was a function of both the laminating resin and the gel coat used. However, the area affected by the blisters was similar in all cases. The size of the blisters depended on the laminating resin used. The chemistry of the materials are complex and variations were seen among generic types from different manufacturers.

12. It is recommended that boat manufacturers institute programs of quality control and quality assurance, with specification for their supplies, to minimize the blister problem.

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