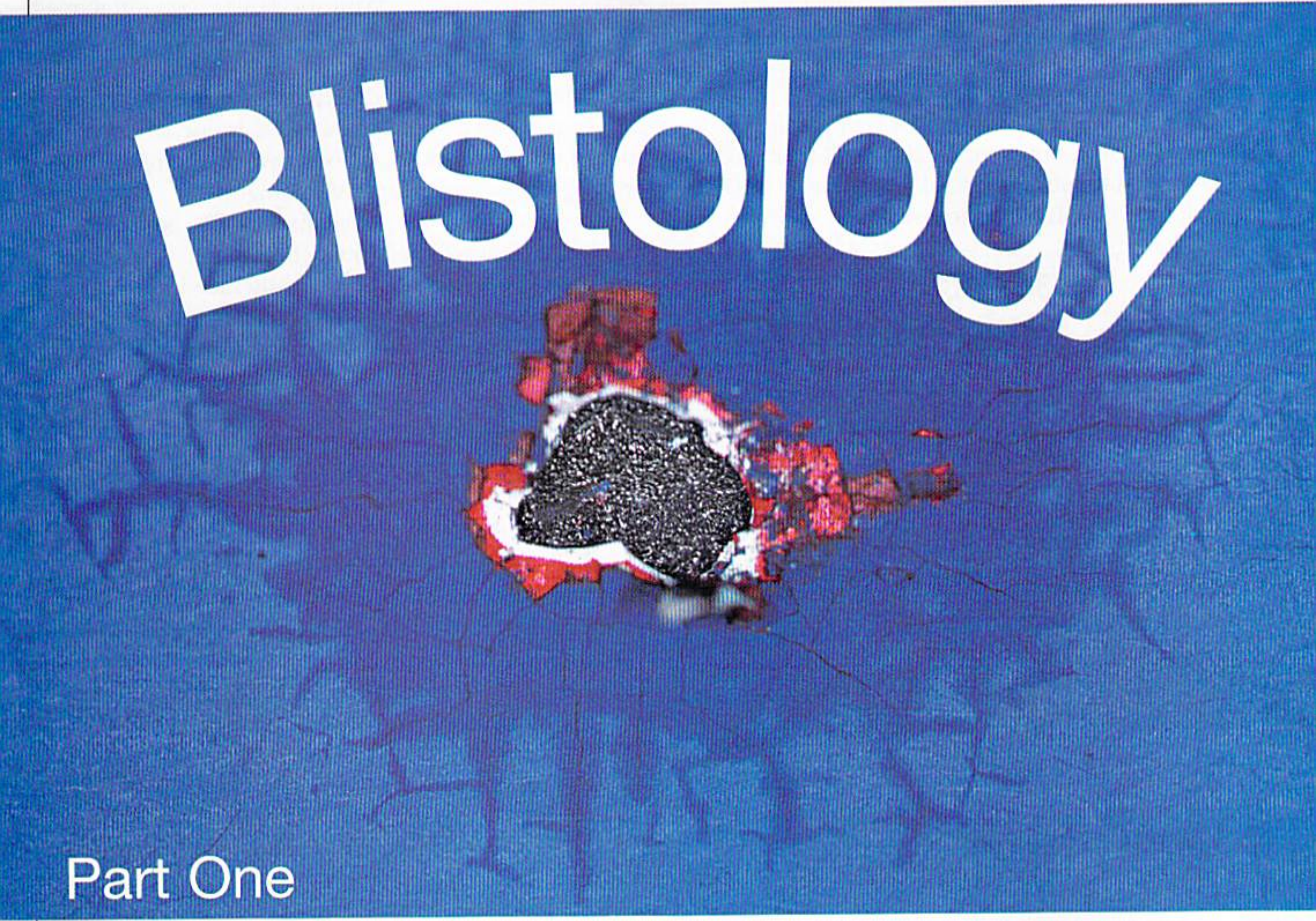
# Blistology

## Part One



## The Chemistry And Formation Of Blisters

Story And Photography By STEVE C. D'ANTONIO

In the first of this two-part series on the subject of fiberglass blisters, we'll explore the basics of production boatbuilding and the different types of resin, glass fabrics, and boatbuilding techniques—and the role they play in the formation of fiberglass blisters.

In the 18 years that I've worked in and managed boatyards, I've encountered few repair subjects that strike as much fear into the hearts of boat owners as that of hull blisters. To an extent, their fear is well placed. Hull blisters, sometimes referred to as osmotic blistering, are a serious problem. Under some circumstances, these blisters may even weaken a vessel's fiberglass laminate. One thing is certain: A case of hull blisters will compromise the marketability and value of most boats. Just ask any broker, or someone who has had to sell a boat that had blisters.

Whether this devaluation is valid remains fertile ground for discussion, primarily because experts continue to disagree about just how much osmosis weakens a laminate. And, in my experience, the degree of compromise varies wildly from boat to boat.

The lack of visible fiberglass reinforcement in this broken blister dome is an indication that osmosis is occurring in the gelcoat. This is no guarantee, however, that the laminate beneath is not similarly affected.

## RESEARCHER BEWARE

The impetus for this article stems from a letter to the editor I read in a popular boating magazine a few years ago. A couple, owners of a boat afflicted with blisters, lamented the dearth of information about the causes of, and solutions to, osmotic blistering. Before we delve into this subject, let the reader be warned. In reality, there is no such scarcity of information on the subject of osmosis causes and repairs. Much of the wealth of information on the subject can be found on the Internet. Unfortunately, a great deal of this information is flawed, inaccurate, or purely anecdotal.

Anyone can create a web page or post authoritative-sounding tomes on this and many other marine subjects. So when researching a subject, remember to consider the source: Books and magazine articles published by experienced, respected experts are usually vetted by equally experienced editors, while many websites are not. This is not to say that there isn't a great deal of accurate information available on the Internet on the subject of osmotic blisters. There is, and much of it originates from university researchers, chemical engineers, and manufacturers of fiberglass resins and composites.

Simply put, if you are faced with a case of fiberglass blisters, first research carefully, and resist the temptation to accept solutions based solely on cost. Be sure to also consider the expertise of the person doing the repair and which repair techniques have a proven record of success.

## IN THE BEGINNING

To understand the process of osmosis and fiberglass blistering, first you need to understand how the conventional production fiberglass boat is, or at least was, built. While this process has progressed over the years, with the exception of improved materials and shop practices, it has remained essentially unchanged for decades.

Polyester resin, the primary component of fiberglass boat construction, was invented in the mid-19th century by a Swedish scientist, Jöns Jacob Berzelius. However, the material was not used commercially until WWII. When the Japanese invasion of Far Eastern territories cut off supplies of natural varnishes used for electrical insulation, polyester resin made from the then-readily available raw materials of oil and coal filled the gap. In the 1950s, when polyester resin was combined with glass filament made by Owens Corning, fiberglass-reinforced polyester (or FRP, as it is known within the industry) boatbuilding was born.

## FIBERGLASS BOATBUILDING

Unlike most timber and alloy vessels, which rely on the construction of an internal grid or skeleton frame structure over which a skin is applied, FRP is essentially built from the outside in, using a female mold. In short, the mold provides the shape of the part, in this case, the hull, but in reverse. Initially, a thin layer of gelcoat is sprayed into the waxed mold. (The wax helps to release the completed fiberglass part from the mold.) After the gelcoat has partially cured, a layer of resin is applied, which achieves an all-important chemical bond with the gelcoat.

Next, a layer of fiberglass, usually in the form of a thin, nonstructural mat (also known as the skincoat), is applied. This layer, which prevents print-through—a telegraphing of successive weave patterns of structural glass laminates—is followed by more resin. Additional, thicker layers are applied to provide structural rigidity, and so on. The result is what's known as a fiberglass laminate. Fore and aft stringers, bulkheads, or unified grid pans or liners may be installed, adding rigidity and facilitating installation of furniture and machinery.

Many other factors and techniques may be involved in the complex process of laminate layup, including the addition of core, vacuum bagging, resin infusion, post-curing, and so on. (Look for a future *PMM* article on the subject of core and composite boatbuilding techniques.) However, what I have described above is the established process, and many boats continue to be built in exactly this manner.

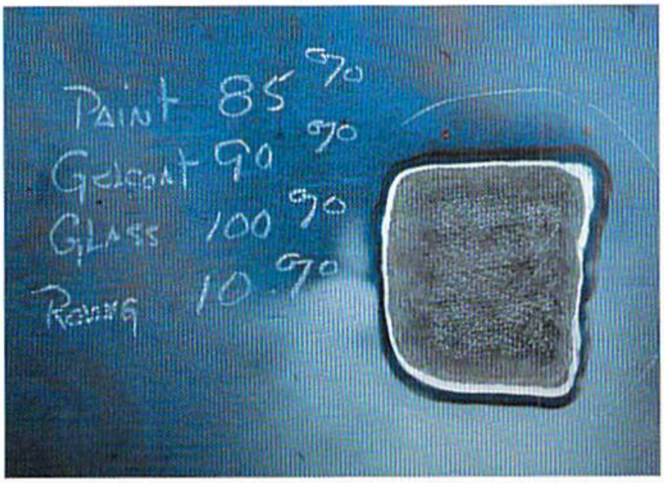
Another critical factor in any FRP lamination is timing—when and how quickly steps are completed will determine whether proper molecular bonding of resin layers is achieved. Miss the chemical window, and what should be an extremely strong primary bond becomes a substantially weaker, and potentially more water absorbent, secondary bond. This is a particularly so for the gelcoat-to-skincoat bond.

The fiberglass-reinforced polyester construction process uses several basic (and a few complex) components. Once again, to understand the process of fiberglass blisters, you must understand these terms and materials.

Gelcoat is simply pigmented resin. In the early days of FRP boatbuilding, many manufacturers thought that gelcoat would provide an impermeable barrier to water (more on why this is important later), although few had any idea of the importance of this feature at the time. Additionally, gelcoat was billed as being so hard and slick that barnacles would be unable to keep their grip, thereby eliminating the need for antifouling paint. As history has proven—rather quickly on the need for antifouling paint, and more slowly on the impermeability of a gelcoat barrier, neither of these claims was true.

The realities of gelcoat are that it provides a relatively stable, aesthetically attractive finish but one that, under even the best of circumstances, presents only a modest barrier to water penetration. The ideal thickness for gelcoat is between 20 and 30 mils (20-30 thousandths of an inch). A thickness less than this will not provide adequate coverage or quality of finish, while gelcoats any thicker than 30 mils are prone to cracking.

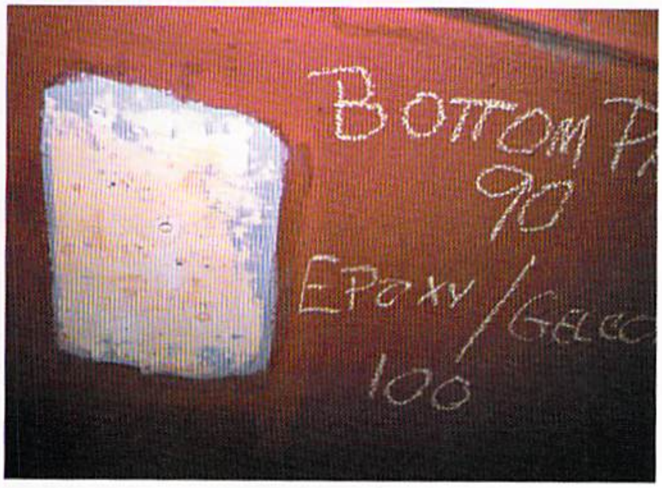
The resin, the glue that binds the FRP structure together, may take several forms. Even today, most boats typically are manufactured using general purpose polyester-based resin. The subcategories of polyester resin (or PE) are orthophthalic and isophthalic (ortho and iso in industry-speak), which simply refers to the type of acid from which these resins are manufactured. Without delving too deeply into the chemistry of these resins, the former is less expensive and less resistant to blistering or osmosis, while the latter is, predictably, more expensive and more resistant to osmotic attack. Because gelcoats are resin based, they are also ortho and iso based—the latter sharing the same attributes of blister resistance with iso-based polyester general purpose resin, and thus the current preference. Nearly all older boats were made using ortho-based resin and gelcoat. (The demarcation line varies, with most builders making the switch from ortho-based resins to iso-based resins sometime in the 1980s.) Unfortunately, some boatbuilders continue to use ortho-based rather than iso-based resins and/or gelcoats.




Left: A barnacle's eye view of a blister. The dome of this blister has been broken, revealing fiberglass filaments, probably chopped-strand mat (or CSM) in this case. Right: The results of a patch test tell the whole story, not a very bad one in this case. The outermost layer of fiberglass laminate is saturated; however, the layer beneath is relatively dry. The percent symbols are a misnomer, these figures are representative of a relative rather than a percent scale.

A relative newcomer to the resin scene, vinylester has proven to be superior to its cousin, polyester, in nearly every way. (There is, however, a price to be paid for this superiority; vinylester costs about 15 percent more than polyester.) Vinylester (or VE) resins are extremely tough and elastic while also embodying excellent permeability characteristics. Another valuable trait of VE resin is its compatibility with polyester resin. The two may be used virtually interchangeably and in direct contact with each other—with the same application equipment and catalysts. As a result of these attributes, VE resin is now preferred by high-quality hull manufactures for either their entire laminate schedule or for the outer layers of the hull. Using VE resin on the outer layers alone, called skin coating, is an acceptable method of preventing osmotic blistering. The skin must be a minimum of about 1/10 of an inch thick, which usually calls for two laminates or layers of fabric and resin.

Finally, epoxy resin has gained favor in the boatbuilding industry as a high-quality, extremely strong material that is also virtually impermeable. Additionally, it is more environmentally friendly than ordinary polyesters and vinylesters, thanks to the low emissions produced during its cure cycle. Epoxy is by far the most expensive of the available boatbuilding resins, and it is acknowledged by manufacturers as somewhat more difficult to work with.




Left: This patch test reveals a previous unsuccessful blister "repair" using the spot repair, drying, and barrier coat technique. Unfortunately, the wet laminate was left behind, and the blisters themselves, the remains of which can be seen, were only ground out and filled. Right: Peeling an osmotically challenged bottom often reveals voids and delaminated areas, which must be repaired before relamination can commence. This is yet another reason to avoid the "blister repair by drying" approach.

Saturating glass fabric with epoxy is more time consuming and difficult than ordinary poly and vinylester. As a result, it is usually used where high strength and/or low emissions are required. It is worth repeating: Epoxy laminates are among the strongest and most blister-resistant structures.

However, epoxy is not readily compatible with poly and vinylester resins; nor is it compatible with glass fabrics whose binders and coupling agents (materials that hold the fabric together and promote resin bonding, respectively) are formulated for poly and vinylester. This resin must be used *only* with epoxy-approved glass fabrics.

Glass fabric reinforcement is available in scores of configurations, sizes, and weights. The individual filaments used to weave different types of glass for FRP construction are gossamer indeed, approximately 1/10 of the thickness of a human hair or about .0002 inch. The principal types are chopped-strand mat, woven roving, and cloth. There are other more exotic fabrics, such as knitted and biaxials, but most boats, particularly those that are suffering from blisters today, are built with these three primary materials. All are used in different applications and for different desired results and require different additives to bind their strands together.

From the standpoint of osmotic blistering, the most relevant fabrics are the ones used just beneath the gelcoat, typically the chopped-strand mat and roving. Mat, which is made up of short (about 2-inch), random lengths of glass filaments, is not as strong as the heavy, rug-like weave of woven roving; however, mat is soft and sponge-like and absorbs resin readily, and as such works well for bonding to other types of glass.

Chopped-strand mat (or CSM) comes in roll form and is held together by additives, known as binders or sizing agents, which are designed to dissolve in resin. To work effectively with polyester or vinylester resin, glass fabrics must be treated with these agents to keep the fabric bound together until it is wet-out with resin.

The ability of a binder to hold the fabric together makes it easier to apply the mat in irregularly shaped locations. Binders are needed primarily for CSM fabrics because they are made up of short, random fibers. We'll talk more later about this additive and the role it plays in the blister process.

Finally, because glass is a relatively slick surface, another agent, known as a coupler, is needed to allow the resin to get a grip on the filament.

## WATER, THE UNIVERSAL SOLVENT

Ironically, the hot tub and spa industry faced the osmotic blister problem in the '60s. As it turns out, hot, chlorinated water is the ideal vehicle for promoting osmotic blistering. The industry's response was to get rid of gelcoat altogether, opting for an acrylic-sheet skin instead. Further study revealed that acrylic is actually more permeable than good gelcoat that's applied in the proper thickness. The key to the acrylic skin's success for the hot tub folks was the absence of water-soluble materials (WSMs). As we'll see, water-soluble materials are the primary villain in the fiberglass blister saga.

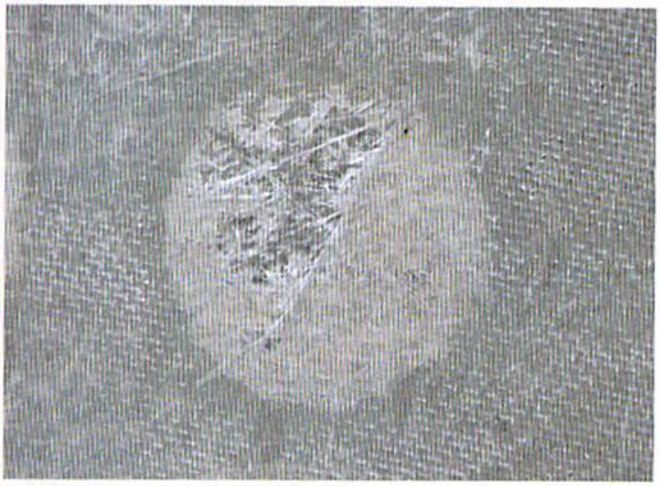
In simplified form, the chemical processes that must occur for blisters to form are as follows. Water-soluble materials must be present beneath a semi-permeable membrane—in this case, the membrane is the gelcoat or outer layers of fiberglass laminate or FRP. Water molecules, which are comparatively small and slippery, find their way through the molecular gaps in the gelcoat and fiberglass laminate, where they encounter WSMs. It's love at first sight and marriage ensues, but the offspring are anything but cute.

As with any relationship, here's where it gets a bit tricky. Some composite experts believe that many of the resin components that have the potential to become WSMs—for example, the binders and couplers mentioned above, as well as thixotropes such as fumed silica, which prevent resin from being too thin and runny—and to be involved in the osmotic process do not present a problem in the laminate immediately after the vessel goes into service. Rather, it's only after long-term immersion that the process of hydrolysis (also known as Le


Vinylester resin, while not a panacea, is essentially the primary solution or ingredient for prevention of osmotic blistering.

Châtelier's principle) begins to work on the laminate, actually taking apart the resin matrix molecule by molecule. As a result, water-soluble components begin to appear in the laminate.

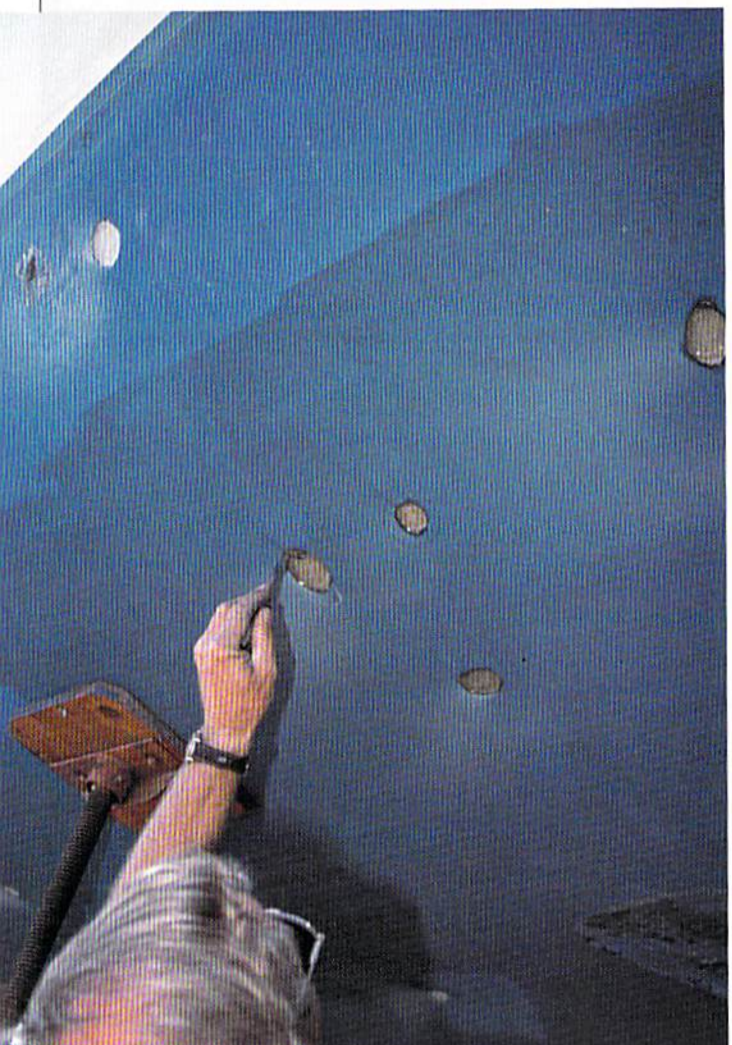
The next process, the actual cause for the blisters themselves, then takes over. According to Thomas J. Rockett, PhD, a research professor at the University of Rhode Island and coauthor of the U.S. Coast Guard-funded study "The Cause of Boat Hull Blisters," water molecules enter the laminate via a process known as permeation. (Nearly all plastics, including FRP, are permeable to some degree.) This, in and of itself, is not a problem as long as the water doesn't react with anything on its journey through the laminate. The difficulty occurs when the water encounters a reactionary agent, such as a WSM. Rockett describes the osmotic process as such: "Water molecules can pass through this layer ["this layer" refers to a semi-permeable membrane, the gelcoat and laminating resin], but the WSM molecules



Top: Blister juice, which frequently has a vinegar-like odor and often consists of a mixture of glycol and acetic acid is seen running out of these recently exposed blisters. The acetic acid is corrosive to resin. Above: A closeup view of a blister base that's been exposed after peeling. The base of a blister may be considerably larger than its visible peak, somewhat like an iceberg, the majority of whose mass lies beneath the surface.

cannot [because they are larger than water molecules]. Since the outside water and the solution are of different concentrations, water will permeate through the gelcoat, in an attempt to dilute the droplet of solution trapped in the laminate. During this process, more water enters the droplet, causing it to expand and create pressure on the surrounding hull material. [This is what forms the blister that's visible on the surface.] It takes place whenever two solutions of different concentrations are surrounded by a semi-permeable membrane. When the pressure exceeds the deformation point of the hull material, it begins to flow or crack. This decreases pressure and allows more space for water to be drawn into the solution."

From this description, one can clearly see that the blister is the final step in the hydrolysis/osmosis problem. The water-soluble materials coupled with permeability and the resulting susceptibility of the resin matrix to hydrolysis appear to be the real culprits. Thus, one could conclude that the primary cause for osmotic hull blistering is the presence of the WSMs, although this borders on oversimplification, because the WSMs are just one of several factors that must be present for osmotic blistering to occur. In fact, these WSMs are necessary evils. As previously mentioned, couplers allow resin to stick to glass filaments. Binders used in some chopped-strand mat and combination mat/woven/knitted fiberglass cloth products, particularly those binders applied as an emulsion, a popular technique in the '70s and early '80s, have also been identified as having strong WSM potential. Additionally, thickening agents or thixotropes such as fumed silica, which are added to resin to increase its viscosity (resin that's too thin will simply run out of a laminate), are also water soluble.



The piecemeal approach to blister repair, individually grinding and filling each blister, is strictly a cosmetic approach, which addresses the symptom rather than the cause of the problem.

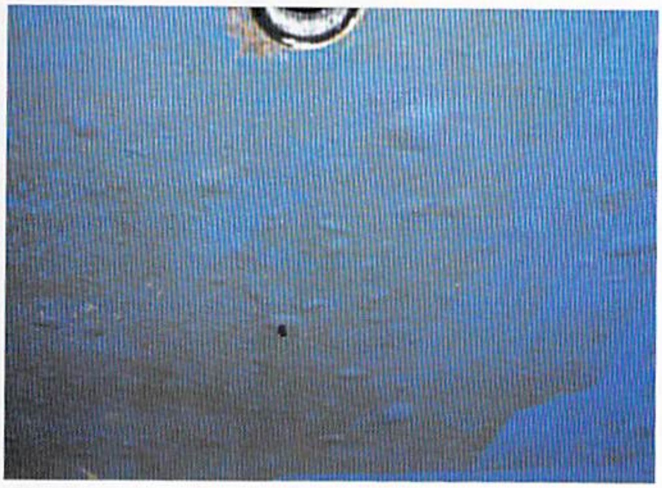
Adding insult to injury in the blister formation story is the recent release of research indicating that heavily stressed fiberglass laminates are more prone to osmosis than their less-stressed counterparts. This makes sense, because stressed laminates tend to microfracture. (Sometimes, the fractures aren't so small. Ever see gelcoat cracks around on-deck hardware, cleats, chain plates, and so on?) These small fractures allow water to enter the laminate more quickly than if the water had to take the normal route through even a semi-permeable gelcoat. Thus, it appears that where FRP strength is needed most, at the keel or adjacent to rudder and strut attachments, is where osmotic action may be most aggressive.

Studies also show that osmosis is accelerated considerably in warmer water. For instance, osmotic blistering appears to occur in Florida with greater regularity than in Maine. Beware, however, of quick analyses from armchair chemists using anecdotal evidence. For example, the word on the street is that boat A blisters badly, while boat B hardly ever gets blisters. But if boat A was manufactured in Florida, most units were sold in the Southeast and, because of its design, it's not used in colder climes. So boat A is certainly more prone to blistering because of design and environmental factors. Boat B, on the other hand, was made using similar materials and manufacturing processes but in New England, where it's heavily marketed. Because of its design, boat B is well suited for rougher, colder waters, so it may show far fewer examples of osmosis.

Add to this already complicated scenario a further wrinkle. Evidence appears to suggest that prolonged immersion accelerates hydrolysis and the osmotic process. Thus, boats used and stored in the northeastern United States or the Great Lakes, where the climate dictates seasonal hauling, are less likely to suffer from blisters than their tropical and subtropical brethren, regardless of laminate makeup. Simply put, periodic hauling, which facilitates some drying of the gelcoat, tends to stave off or at least delay the onset of osmosis.

There remains some disagreement on the subject of frequency of osmosis occurrence in fresh water versus sea water. Some believe that osmosis occurs more quickly in fresh water than in salt water, while others believe it's the reverse. The group pointing to sea water also points out that salts (not just sea salt or sodium chloride, but a vast array of ionic compounds created during a combination of elements) promote osmotic reactions. Science and history, however, would appear to be on the side that believes accelerated osmosis occurs in fresh water because it is less dense than sea water and thus permeates semi-permeable membranes with greater ease.

Again, anecdotal evidence can be misleading. While osmotic blistering does occur in the Great



The first sign of osmosis is usually the appearance of blisters. While the quantity and size of the blisters is often an indication of the severity of the problem, a patch or lab coupon test is the only way to be certain of how deeply the laminate is affected.

Lakes, it is far less common on a per capita basis than osmosis in the southeastern United States. However, the Great Lakes are cold and they do freeze over, requiring that boats be hauled every winter, which facilitates drying of the bottom.

Resin manufacturers and laboratories that carry out osmosis resistance tests nearly universally use hot, sometimes boiling, fresh water to accelerate testing. A wet door mat saturated with rainwater and left on a gelcoated surface will cause blistering, sometimes in a matter of weeks. Experience shows, however, that regardless of the rate, osmosis occurs in both fresh and seawater environments.

In Part Two of this two-part series, we'll explore the details of what happens to an osmotically challenged hull, the chemistry of how the hull may be weakened, moisture testing, and osmosis repair and prevention.