FIBERGLASS MATERIAL SPECIFICATION TEST SUPPORT

to

U.S. COAST GUARD
DEPARTMENT OF TRANSPORTATION

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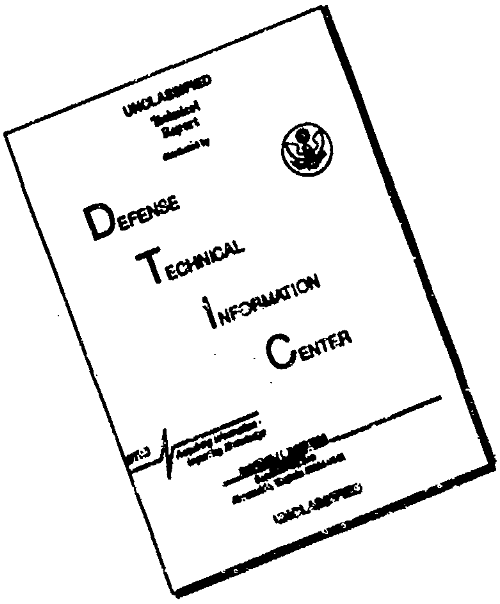

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FIBERGLASS MATERIAL
SPECIFICATION TEST SUPPORT

by

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SUMMARY

Battelle has conducted a preliminary investigation for the U.S. Coast Guard to establish an information baseline into possible causes for the blistering of gel coat laminates on boats.

To accomplish this task, Battelle divided the program into two parts: a computer-aided literature survey and sample analysis.

The purpose of the literature survey was threefold: (1) identify the extent of the problem, (2) determine what other research has been done in the past; and (3) determine if any information exists from other fields of interest that may relate to the blistering problem.

The purpose of the sample analysis task was to confirm or refute information found in the literature survey and to aid Battelle in forming hypotheses on the causes of blistering.

The literature survey covered six data bases between the years 1980-1985. A total of 246 abstracts were reviewed and 38 articles were selected for full review.

For purposes of discussion in this report, survey results have been divided into four areas: (1) extent of problem; (2) mechanics of blister formation, (3) suspected causes of blistering, and (4) accelerate testing.

According to the literature, estimates on the extent of the problem vary with the source, but for boats that spend most of their time in the water, estimates are as high as 20-48%. Newer boats appear to have a greater incidence of blistering and some estimates state that 80% of all boats now being built using glass

reinforced polyester will eventually experience some degree of blistering.

It appears to be generally agreed that osmosis (diffusion) is the predominant mechanism for the onset of blister formation, but little agreement is found beyond that. The suspected causes of osmosis are reported to be caused by either physical or chemical debonding between the laminates or between the gel coat and the laminate. In physical debonding, water permeates through the gel coat into an interface. At some point, an osmotic gradient is set up and more water is pulled into the area which will eventually form a blister. ~~It was~~ also found that chemical debonding may be caused by hydrolysis (breaking a chemical bond and adding water) of the glass at an interface, thereby breaking the chemical bonds and setting up an osmotic cell. (JFS)

It is apparent that there is probably no single cause of blistering. Groups who have studied blister formation are divided between those who say there is a problem with the materials used or the formulation of the resin, and those who say that the problems stem from faulty fabrication techniques. In reality, blistering may well result from either, or a combination of both. Literature on the causes of blistering could be logically divided into four areas (resin, reinforcement, formulation, and fabrication) and this organization is carried into the present report.

Early blistering in the life of a boat hull is often attributed to the shortcomings of the gel coat. It is held that gel coat blistering occurs at a rate directly dependent on the permeability of the gel coat to water. The suggested solution is to select a gel coat with known minimum water permeability. Another reported cause was the presence of excess glycol in the resin. This permits the polyester to become more permeable to water as well as furnishing a solute (dissolved substance) to promote osmosis.

Several groups have previously studied both binders and reinforcement factors. A common binder used in emulsion-bonded mats is polyvinyl acetate. This compound can hydrolyze to form acetic acid, which has been detected in fluid taken from blisters in this type of mat. Other studies indicate that using a glass more resistant to hydrolysis reduces blistering.

Several studies have been conducted on the effect of changing catalysts and concentration in resins during fabrication. Catalyst and accelerator residues have been found in blister fluids. Since most can be converted to water-soluble materials and do not become an integral part of the matrix, these can also contribute to the problem of osmosis.

Many groups hold the opinion that the blister problem has its roots in the fabrication processes. As evidence, they point out the fact that blistering is fairly random.

The U.S. Coast Guard provided Battelle with two blistered samples from the same fiberglass boat. Therefore, it is possible to draw conclusions pertaining to the specific fiberglass reinforced polyester marine laminate examined, but this information may not be generally applied until more samples can be analyzed. Battelle conducted four analytical tests on these samples:

- Differential Scanning Calorimetry (DSC)
- Thermomechanical Analysis (TMA)
- Thermogravimetric Analysis (TGA)
- Gel Permeation Chromatography (GPC).

All data obtained from these studies support the general conclusion that the two blistered samples provided by the USCG were undercured.

DSC data obtained from 12 samples (representing the two blistered hull areas) consistently exhibited endothermal reactions. These reactions are believed to represent a continuation of the curing process, thus identifying the probable cause of blistering of these samples as undercuring.

TGA data offer direct evidence of non-homogeneity of the blistered samples. Glass fiber content varied 20 percent between bow and stern samples suggesting poor glass dispersion. Low temperature volatiles, presumably water, varied significantly. All gel coat samples contained up to 0.3 percent water.

TMA data support the contention that the samples are not homogeneous in nature, thus pointing to variability in fabrication and cure. Non-homogeneity will cause concerns beyond cosmetic problems and may ultimately result in loss of structural integrity.

GPC data indicate a partially reacted system because of the presence of high molecular weight species, probably unreacted oligomer.

Based on information obtained from the literature and the limited data obtained from two blistered samples, it can be concluded that the basic mechanism associated with blistering is osmosis or diffusion. Battelle researchers also believe that:

(1) The FRP blistering problem is undoubtedly due to one or more of the factors which influence the quality, composition, and construction of the composite

(2) Materials specifications and quality control procedures to minimize introduction of non-reactive (osmosis promoting) components into resin formulations need to be established or promoted

(3) Procedures need to be established or promoted to provide continuous monitoring of resin formulations and production variances. This could be visual (color based) or recorded flow rates with out-of-ratio alarms.

(4) Precautions should be promoted to eliminate fabrication practices which adversely affect construction quality (such as uncoordinated spray of either catalyst or resin on construction or contact of catalyst with glass instead of mixing with resin).

Drawing upon the information obtained from conducting this study, the Battelle research team offers the following recommendations to pursue the resolution of the blistering problem.

(1) Conduct a parametric cure grid to determine the critical factors associated with blistering. This would elucidate the factors and interrelationship of factors most responsible for deficient interlaminar cures. Factors should include all formulation variables, time, temperature, and humidity, processing variables, etc.

(2) Establish a fabrication quality control procedure coordinated to the actual construction. This could be small reference panels made in parallel with actual construction. These could be used for various property determinating either as fabricated or historically.

(3) Conduct unbiased on-site observations of materials handling, quality control, and boat construction to evaluate potential for formulation/fabrication variances.

(4) Provide additional blister samples for cure determinations if the USCG desires to confirm data cited in this report which are based on very limited observations. This would also provide a much-needed data base for the GRP-blistering problem.

INTRODUCTION

Background

The blistering of gel coat laminates on boats and other composite products exposed to water has been observed for a number of years. Blistering has been found to occur under various conditions, with different resin systems and composite materials, different catalysts, cure mechanisms and schedules. A great number of hypotheses have been proposed to explain blister formation; however, experimental data and verification have not been definitely correlated and evaluated.

Battelle submitted a three-phase proposal addressing fiberglass blistering to the U.S. Coast Guard in the fall of 1984. This proposal was designed to:

(1) Establish a sound base by information acquisition

(2) Conduct minimum laboratory evaluations which would involve key experiments to answer and resolve questions involving blister formation, identification, and correction

(3) Conduct field testing which would include implementation of quality control procedures.

The U.S. Coast Guard expanded the scope of the program and authorized a preliminary investigation directed toward ultimately determining if blistering of the gel coat causes structural problems or just cosmetic problems. This report addresses the preliminary program just completed.

Program Objectives

The objectives of this program are (1) to investigate the influence of gel coat, cure mechanism, and extent of cure on the tendency of the boat hull to blister and (2) to obtain and examine relevant information which may provide a basis for a practical quality control standard which could be used by the U.S. Coast Guard.

Technical Approach

To accomplish these objectives, the program was subdivided into two tasks:

- Literature search
- Sample analysis.

The purpose of the literature survey was threefold: (1) identify the extent of the problem; (2) determine what other research has been done in the past; and (3) determine if any information exists from other fields of interest that may relate to this problem.

The purpose of the sample analysis task was to confirm or refute information found in the literature survey and to aid Battelle in forming hypotheses on the causes of blistering.

The Coast Guard provided Battelle with two core samples for analysis which were cut from one blistered fiberglass boat hull. From the information gathered from these two tasks, Battelle was to identify probable variables that may impact on the blistering problem and identify, if possible, effective repair and prevention techniques.

LITERATURE SURVEY

The literature survey was conducted using key words selected by Battelle's research team, with the aid of the Battelle librarian. The computer-aided search included six data bases:

- Engineering Meetings
- Engineering Index
- Chemical Abstracts
- U.S. Patents
- World Patents
- NTIS.

Key words were divided into two groups. Group A was used to identify the fields and Group B was used to narrow the fields by comparing Group B against Group A and selecting those abstracts that responds to both groups (Table 1).

TABLE 1. KEY WORD LIST

Group A	Group B
osmosis	fiberglass
permeation	marine
blister(s)(ing)	boat(s)(ing)
osmotic pressure(s)	gel coat(s)
water diffusion	polyester glass
	polyester
	reinforced plastic(s)
	laminate(s)

The comparison of key words--Group B against Group A--generated 246 responses for the period between 1980-1985. The survey was limited to these years in order to avoid redundant and outdated information and to keep the number of responses to a manageable level. The abstracts of these articles were reviewed and 38 articles were selected for full review. Of these articles, 33 were found to be of value, and 4 of the most informative are included in Appendix C. A complete list of titles reviewed and used in the report are provided in Appendix D and copies of all the articles are being provided under separate cover.

Survey Results

For purposes of discussion, survey results have been divided into four areas: (1) extent of problem; (2) mechanics of blister formation, (3) suspected causes of blistering, and (4) accelerated testing. Suspected causes are further divided into four groupings: (1) resin factors; (2) reinforcement factors; (3) formulation factors; and (4) fabrication. A final section addresses accelerated testing. A logical repair procedure is cited by Myhre(22) and Olford(25) and this is reproduced in Appendix A of this report.

Extent of Problem

Estimates on the extent of the problem vary with the source, but for boats which spend most of their time in the water, one domestic source states that blistering affects 20-48%.(8) Another source indicates that industry figures show an incidence of blistering in 10% of boats now being built.(8) Boats which are removed from water after use or removed seasonally appear to be affected less; reportedly between 0.5 and 5%. Newer boats seem to have a greater incidence of blistering and one report states that 80% of all boats using glass reinforced polyesters (GRP) will eventually experionce some degree of blistering.(8)

Mechanics of Blistering

Osmosis (diffusion through a semi-permeable membrane) is thought to be the predominant mechanism for the onset of blister formation, although capillarity in conjunction with diffusion may be equally involved. This was demonstrated in a study where test panels were doped with soluble salts. The doped panels showed greatly accelerated blistering when subjected to immersion in fresh water. Immersion in a saturated salt solution appeared to inhibit blister formation as would be expected if osmosis were the mechanism of attack.(15) Since virtually all polyesters are permeable to water, it appears that water diffuses through the gel coat into an interface, either between the laminates or between the gel coat and laminate. Soluble material may be encountered at the interface, or carried there by the water. At some point, an osmotic gradient is set up and more water is pulled into the area which will eventually form a blister.(3,25) The blister first appears as a plane of delamination.(7) As more water is pulled in, the delamination continues and osmotic pressure within the delaminated area causes a blister to form. Some of these blisters have an internal pressure of 5 to 6 atmospheres.(25) Kinetic studies have shown this to be sufficient pressure to cause separation between laminates.(29)

It is generally accepted that freshwater glass reinforced plastics (GRP) boats have more serious problems with blistering than their saltwater counterparts; but a survey of GRP boat owners, conducted by "The Practical Sailor", indicated that those boats which were sailed in saltwater had more problems.(26) It is thought that this is because most recreational boaters in freshwater areas drydock their boats during the winter months.

It has been observed(16) that newer boats seem to have a greater problem with blistering than many older ones. At least one report attributes this to modern spray-up techniques which have replaced the "bucket and brush" method of laminate lay-up. These spray-up techniques can reportedly cause non-uniform delivery and/or mixing of catalyst. Local concentrations of water-soluble catalyst will cause debonding at that site and lead to the formation of an osmotic cell as water diffuses into the site. (16) This is an example of physical debonding. If this were the sole reason for osmosis, it would seem that once a solute was diluted, blister growth would stop. However, there appears to be a chemical reaction which accelerates blister formation by furnishing more solute to keep the osmotic cell going. Another report states that the debonding process occurs when swelling of the polymer, due to water absorption, exceeds the shrinkage due to cross-linking. This causes localized stresses which combine to physically break the bond between glass and resin.(17)

Several of the reports reviewed state that the onset of blistering is due to chemical debonding between the resin and glass fiber.(2,7,18,25,30) This could be due to hydrolysis of the glass, sizing, or resin.

During hydrolysis of the glass, water reacts with cations in the fibers producing hydroxyl ions. The concentration of hydroxyl ions will slowly increase to a concentration which will begin degradation of more fibers.(18) The blisters often contain slightly acidic fluid.(6,15) The acid probably arises from the breakdown of polyvinyl acetate to acetic acid and the oxidation of styrene to benzoic acid. The ester linkages of the resins are also vulnerable to hydrolysis.

Suspected Cause of Blistering

There is probably no single cause of blistering. Groups who are studying blister formation are divided between those who say there is a problem in the materials used or the formulation of the resins(3,7,10,15-20) and those who say that the problems stem from faulty fabrication techniques.(9,13,16,18,20,25) In reality, blistering may well result from any single factor or any combination thereof. Four areas encountered in the literature (resin, reinforcement, formulation, fabrication) are discussed below.

Resin Factors. Several sources attribute early blister formation to shortcomings of the gel coat.(3,23,25) It is held that gel coat blistering occurs at a rate dependent on permeability of the gel coat and suggests that the gel coat should be of minimum permeability.(11) Most who address the issue agree that isophthalic neopentyl glycol gel coats provide superior protection. These resins have a reduced accessability to the ester linkage due to stearic hindrance and are more fatigue resistant than orthophthalic resins.(3) Also, isophthalics with a higher heat distortion temperature performed better, but this may be a manifestation which occurs only in accelerated testing in heated water. Pigmented gel coats were generally inferior and will be discussed in more detail later.

Another factor commonly reported as a cause of blistering is an excess of glycol in the resin.(6-9) This makes the polyester more permeable to water as well as furnishing a solute to promote osmosis. This was demonstrated in several cases by purposely adding a slight excess of glycol to either the gel coat or the laminating resin. In each case, the extra glycol (which does not enter into the curing reaction) appeared to dramatically reduce the time to the onset of blistering and also gave rise to larger blisters. In one case, the water in which the laminate was soaked was analyzed and traces of glycol were detected, as well as isophthalic and orthophthalic acids from the gel coat and laminating resins.

Reinforcement Factors. Several groups have compared the use of emulsion-bonded chopped-strand mats (CSM) with powder-bonded CSM.(6,10,15,23,2[illegible]) In the case of emulsion-bonded mats, the binders are usually polyvinyl acetate. This compound will hydrolyze slowly to form acetic acid, which has been detected in blister fluid taken from laminates made with this type of mat. The powder binders are usually bisphenol polyester and are hydrolytically more stable.(15) One report says that the emulsion-bonded mat functioned as well as the powder-bonded mat when an isophthalic-laminating resin and an isophthalic-neopentyl glycol gel coat were used. This is an important factor from the standpoint of the manufacturer, because the powder-bonded mats are much harder to work with. It is more difficult to work air bubbles out of powder-bonded laminates.

In one study, unfilled and glass-filled laminates were carefully weighed and then soaked in water. There was a definite weight reduction in the glass-filled material with no corresponding change in the unfilled material. This strongly suggests that there was some leaching from the glass or coupling agent.(17) Atomic absorption measurements of blister fluids reveal a large concentration of calcium and smaller concentrations of iron and zinc. Presumably, these ions were leached from the glass by water.(15) These results show the need for a fiber that is water and corrosion resistant.

The "E"-glass" fiber (electrical grade) is most often used, but the "S" type (steel grade) is more water resistant and is suggested as a substitute.

In several cases a resin-rich glass veil or woven-roving mat was applied between the gel coat and laminate. This layer was not hard rolled to leave a resin-rich barrier. This increased blister resistance in all laminates, regardless of glass type, resin, or catalyst used.(15,23,24,25)

When studies were made of the bonds at the glass/resin interface, a degree of stress was found. The bonds are covalent between the coupling agent and the silanol groups on the glass. The coupling agent bonds to the resin during curing. It was found that nearly all of these bonds were broken when subjected to boiling water.(17,28) It is suggested that the incorporation of vinyl groups to the coupling agent will improve bonding and hence, improve water resistance.

Formulation Factors. Several studies have been conducted on the effect of changing catalysts and catalyst concentration in resins.(11,12,15,23,24) Catalyst and accelerator residues have been found in blister fluids. Since most can be converted to water-soluble materials and do not become an integral part of the matrix, they can contribute to the problem of osmosis. Cobalt has been found in high concentrations in blister fluids in laminates where it was used as a promoter. This is most obvious when the laminate is in contact with chlorinated water, as in pools and spas. The cobalt in the blister will create a dark stain.

Some reports indicate that decreasing the catalyst and increasing the promoter concentration, to hold the same gel time, will reduce the possibility of blistering and give the same degree of cure.(12,15,25) Another report states further that a common practice among laminators is to add extra catalyst to speed the cure time. This can cause overcure and lead to cracking. Another report says that increasing the catalyst alone will give a faster cure without overcuring. This report cautions against overpromotion.(11) Yet another report says that varying catalyst and promoter concentrations have no effect on the blistering rate.(24) Since most resins are now sold in a preaccelerated form, it was suggested that tests should be conducted on each batch of resin to determine the optimal catalyst content to achieve the desired cure for the given mold shop conditions.(25) Nearly all reports state that carefully following the manufacturer's recommendations is best.

Studies were made of the effects of other additives, such as pigments, thickeners, and fire retardants.(6,10,12,23,25) In each case, these additives accelerated blistering dramatically. One group was able to use a white gel coat because the pigment was dispersed in the resin and not in a low molecular weight carrier. The laminates prepared from this resin performed as well as those made with clear resin.

<u>Fabrication Factors</u>. There are many groups that hold the opinion that the blistering problem has its roots in the fabrication processes.(9,13,16,18,20,25, etc.) As evidence they point out the fact that blistering is fairly random. If the problem were due only to the materials used, the blistering would be more general and regularly spaced.

It has been suggested that the use of wax mold release agents produces a less permeable gel coat.(10,14) Another commonly used release agent is aqueous polyvinyl acetate. It may be that the water in this is evaporating through the laminate and interfering with the cure.

One report claims that the primary cause of blistering is undissolved methyl ethyl ketone peroxide in the gel coat.(16) As evidence, it was pointed out that there are many boats which are 20+ years old made of orthophthalic resins that show no gel coat blistering. Amoco is the only domestic producer of isophthalic acid and this report contends that they may not be able to produce enough to meet the demand for all boats presently being manufactured.(16)

Many newer boats are showing signs of blistering very early in their lives, due perhaps to improper spray techniques. It has become standard practice to press the first stage of the gun trigger of the spray unit to be sure that catalyst is being delivered. This causes local concentrations of catalyst in the molds as do leaking lines and worn seals. This can result in improperly catalyzed resin systems. Colored catalysts and resins containing catalyst-sensitive dyes have been developed so these problems can be visually detected. When a problem is detected, the leak is usually fixed and the drops of pure catalyst in the mold are simply covered by the next layer of laminate. To research this, the content of some blisters was analyzed by gas chromatography and a high level of dimethyl phthalate (DMP) was found. DMP is a carrier for most commercial MEKP catalysts. Although DMP is relatively insoluble in water, a pocket of it would be a probable site of delamination and subsequent blistering.

Another point raised in this report(16) is that the catalyst is often sprayed at an angle such that it contacts the glass before it contacts and mixes with the resin stream. Tests have shown that catalyst applied in this manner cannot be displaced from the glass by rolling. Accordingly, the resin system may be undercatalyzed as well as catalyst-coated glass becoming a potential site for blistering. The author of this report suggests the use of a two-pot resin spraying system where the resin is divided into two parts, one containing benzoyl peroxide as the catalyst, and the other containing N,N-dimethyl aniline. The two mixtures are sent through separate sprayers in a manner that causes the two sprays to impinge on each other. The author of the report notes there are very few companies employing this technique, but he is not aware of any problems with blistering in their boats.

Mold shop temperature is very important. Temperatures below 64°F (18°C) will cause high viscosity, air bubbles (especially with spray application), and uneven thickness during application.(15) Gelation is delayed by low temperatures, so the evaporation of styrene can be excessive, and this can lead to an unsatisfactory cure.(14) Air drafts must be eliminated to insure a uniform cure. The relative humidity must be controlled and kept low. Mixing of the constituents must be done carefully to avoid air bubbles while at the same time assuring a good mix.(15) Care must be taken to keep air bubbles, dust, and moisture out of the layers of laminate.(15) One ply at a time should be applied but, to insure adhesion, the previous ply should be in the correct state of cure.(15) Reportedly, it is common practice to pre-wet two or three mats on a bench and lay them into the mold together, applying more resin as they are being rolled out.(25) It is very easy to introduce large bubbles between the layers and very difficult to work them out. Often, larger bubbles are simply broken into many smaller ones. Each laminate layer should be fully wetted with all air pockets worked out. Air bubbles can be particularly troublesome. Besides weakening the laminate, bubbles furnish a void where absorbed water can gather. This hastens deeper penetration of the laminate and possible problems later. The time between solidification of the gel coat and the application of the first layer of laminate is critical. Air exposure results in a tacky surface. This is due to incomplete cure of the resin surface brought about by inhibition of the cross-linking reaction by oxygen.(15)

Several other reports suggest incomplete cure of the resin as a principle cause of blistering.(14,15,24,25) This problem could be caused by low temperature or high humidity in the mold shop, incorrect catalyst content, or poor postcure condition, to name only a few.

In studies comparing resins with different reactivities, it was found that curing at room temperature had no effect on blister resistance. Curing at elevated temperatures, however, stiffened the laminates using more reactive resins and reduced the tensile elongation to failure.(24) This is presumably because higher cure temperatures promote cross-linking. This is very important to the manufacturer as most polyester laminates are ordered according to stiffness criteria. Too much heat can cause overcure resulting in brittleness and cracking. As mentioned previously, cracking can hasten water absorption.

Postcure is nearly as important as the initial cure. Often, a boat is removed from the curing area to a postcure area or even outside where there is no atmospheric control. This can have a deleterious effect. If the boat were cured at an elevated temperature, it must be cooled very slowly to minimize internal stresses which can lead to cracking. One report suggests postcuring at room temperature for as long as six weeks before applying paint.(25)

In many cases, blistered areas coincided with areas which had low Barcol hardness readings (less than 30).(9,24) This indicates incomplete cure. It has been suggested that Barcol hardness tests be performed on finished boats to determine if there is a danger of blistering. The measured hardness should be at least 90% of the manufacture's recommendations. Also, solvent swabbed on the surface should cause no tackiness. Methyl ethyl ketone should be used for examining epoxy and acetone for polyesters. These tests will give no absolute measurement of a boat's chances for developing blisters, but probably can be used to differentiate between a good and bad cure.

<u>Fabrication</u>. One report states that using the same resin system in the gel coat as in the laminate helped performance by alleviating interlaminar problems.(24) This would have a positive result on blister resistance, since most blisters occur

at an interface. This report states that both the gel coat and the laminating resin should be fairly flexible (2-6% tensile elongation to failure) but not at the expense of chemical or hydrolytic resistance. This would reduce the incidence of cracking and thereby slow water permeability.

Thixotropy of the resins is important to prevent thinning and puddling in the molds. One study was made to try to optimize thixotropic properties.(12) For hydrolytic stability, the molecular weight should be high and the acid number low. However, the viscosity increases with the molecular weight, so viscosity, acid number, and molecular weight must be carefully balanced for ease in spray application. Using fumed silica as a thickener, it was found that the best compromise was reached at a Gardner-Holdt viscosity of T at 60% nonvolatile material and an acid number below 20.

When painting boat hulls, two-pack epoxies and the two-pack polyurethanes appear to work best.(15,25) These paints are good water barriers and give excellent weather resistance. Etch primers should never be used, nor should paint removers be used when repainting. Any paint removal should be done by carefully sanding with about 200 grit abrasive to a matte finish. Primer should then be applied, followed by alternating colors of paint to assure good coverage. For epoxies, the final thickness should be at least 6 mils (0.25 mm). For polyurethanes, the final thickness should be at least 2.5 mils (0.1 mm). Inside surfaces should be painted also, especially in the bilges.

The gel coat should be continued to well above the water line. The thickness of gel coat is considered the most important key to blister resistance in one report. About 10% shrinkage during cure should be expected when designing a final dry thickness of about 12-15 mils (0.5-0.6 mm). Use of a wet film gauge is advocated. Constant thickness is also very important. A thicker gel coat will reduce the chance of "wicking" or capillarity along stray fibers that may protrude into the gel coat from the underlying laminate. This is a valid concern since it is suspected that some of the blisters analyzed in the field were probably caused by this type of mechanism. These blisters are elongated and have a fiber or bundle of fibers in their center. These blisters in particular can provide an avenue for deeper penetration of the laminate by water. Many groups advocate the use of epoxy-based gel coats.(5,14,15) They are much less permeable (as much as 500 times less), less susceptible to hydrolysis, and contain no glycol. Epoxies do, however, contain small amounts of water-soluble anhydrides and dicyandiamides as curing agents. After prolonged periods of water exposure, they are able to absorb more water than polyesters, but much of the water appears to be bound to polar groups in the matrix. Epoxy coated laminates seem to be less prone to "wicking". They are also tougher and not as likely to crack.

As with the gel coat, the general consensus is that isophthalics are the resins of choice for laminating resins.(3,9,19) Since all polyesters are eventually going to be permeated if left in contact with water, it is obvious that the laminating resin must have hydrolytic stability also.

One report suggests that using a laminating resins which is more permeable than the gel coat would reduce the chance of water buildup at the interfaces. It also suggests using a high molecular weight, low acid number resin which is easier to achieve with an isophthalic resin.(15) As with the gel coat, a low glycol content is preferable.

Accelerated Testing

There is some disagreement with regard to how a laminate should be tested. Some researchers have tried to develop accelerated test methods. The most commonly used accelerated test is done in a "turtle box" which is a large, square tank covered with round ports a few inches in diameter. Test panels are held tightly against these ports and hot water is placed in the tank so that one side of the test panels is in contact with the heated water. There is considerable disagreement over the correct water temperature to use in this test. Some use boiling water, some use 150°F (65°C) water, and some use 104°F (40°C) water.

The use of hot water does accelerate the blistering process many times, probably because of a softening of the gel coat.(25) However, it is not possible to correlate results for different resins.(3) Each resin has its own characteristic glass transition temperature (Tg) and its own heat distortion temperature (HDT), among many other temperature dependent characteristics. This can be critical when the laminating and gel coat resins are different types. One report contends that the boiling water test is not valid because results correlate only half of the time and blisters appear to be heat-stress related and not hydrolysis related.(12) Another source says delamination of samples tested in hot water was due to swelling in the polymer or hydrolytic scission of esters. This source contended that delamination occurred at a water absorption level specific for each resin and that there would not have been any effect at ambient temperatures and lower water absorption.(15)

Of course, some method of accelerated testing is needed to get results in a realistic time frame. As a general rule, most chemical reactions will double in rate for every 10°F (4°C) increase, so testing for blister resistance at an elevated temperature can give results much faster (estimated at 5-6 times as fast for 40°C water). However, as the test temperature rises, accuracy and reliability are sacrificed.

Lloyd's Registry of Shipping has made some recommendations to help deal with the problem of blistering. These include:

- Assemble and collate all research and test results related to blistering.

- Subsidize fundamental research projects in the area of blistering.
- Rapidly incorporate new fabrication techniques into industry.
- Close cooperation between researchers, raw materials manufacturers, and builders as needed.

One final point raised is the issue of educating the laminator.(13) Too often in the United States, he is an unskilled laborer. In Europe, boat laminators are generally older and more skilled at their jobs and are considered to be skilled laborers. Also, much of the information which has been made available by researchers has not been used by industry. The reason most often cited is cost.

SAMPLE ANALYSIS

In the early stages of the research program, the U.S. Coast Guard indicated that samples would be difficult to obtain since it would require cutting a hole into the core mat of the boats and most owners did not want to have this done. For this reason, only two samples were obtained from a single boat. Therefore, it is possible to draw conclusions pertaining to the fiberglass reinforced polyester marine laminate examined, but this information may not be generally applied until more samples can be analyzed.

The two-inch-diameter samples, as stated, were taken from the same craft--one from the bow and one from the stern. When the samples were taken, both contained blisters; however, when they reached Battelle, the samples had dried and no blisters were evident.

Battelle conducted four analytical tests on these samples:

- Differential Scanning Calorimetry
- Thermomechanical Analysis
- Thermogravimetric Analysis
- Gel Permeation Chromatography.

Sample Preparation

From the core samples, 5/16-inch-diameter plugs were cut; then the plugs were cut into halves, interior and exterior. Samples were then prepared by cutting slices from the plugs just below the surface of the interior or exterior wall.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a method used to measure any transition that the sample undergoes resulting in the liberation or absorption of energy. In the event that a transition occurs, thermal energy is added to, or subtracted from the sample in order to maintain the sample at the same temperature. Because this energy input is precisely equivalent in magnitude to the energy absorbed or evolved in the particular transition, a recording of this balancing energy yields a direct calorimetric measurement of the transition energy. For example, if a sample were to change in state or undergo an endothermic reaction, the DSC trace might look like Figure 1, trace number "A". If the transition were an endothermic reaction and it was only partially reacted, a second scan could be conducted and it would look something like scan "B". Eventually, if the sample were heated enough times, the reaction would be exhausted and a 100% cure is said to have taken place.

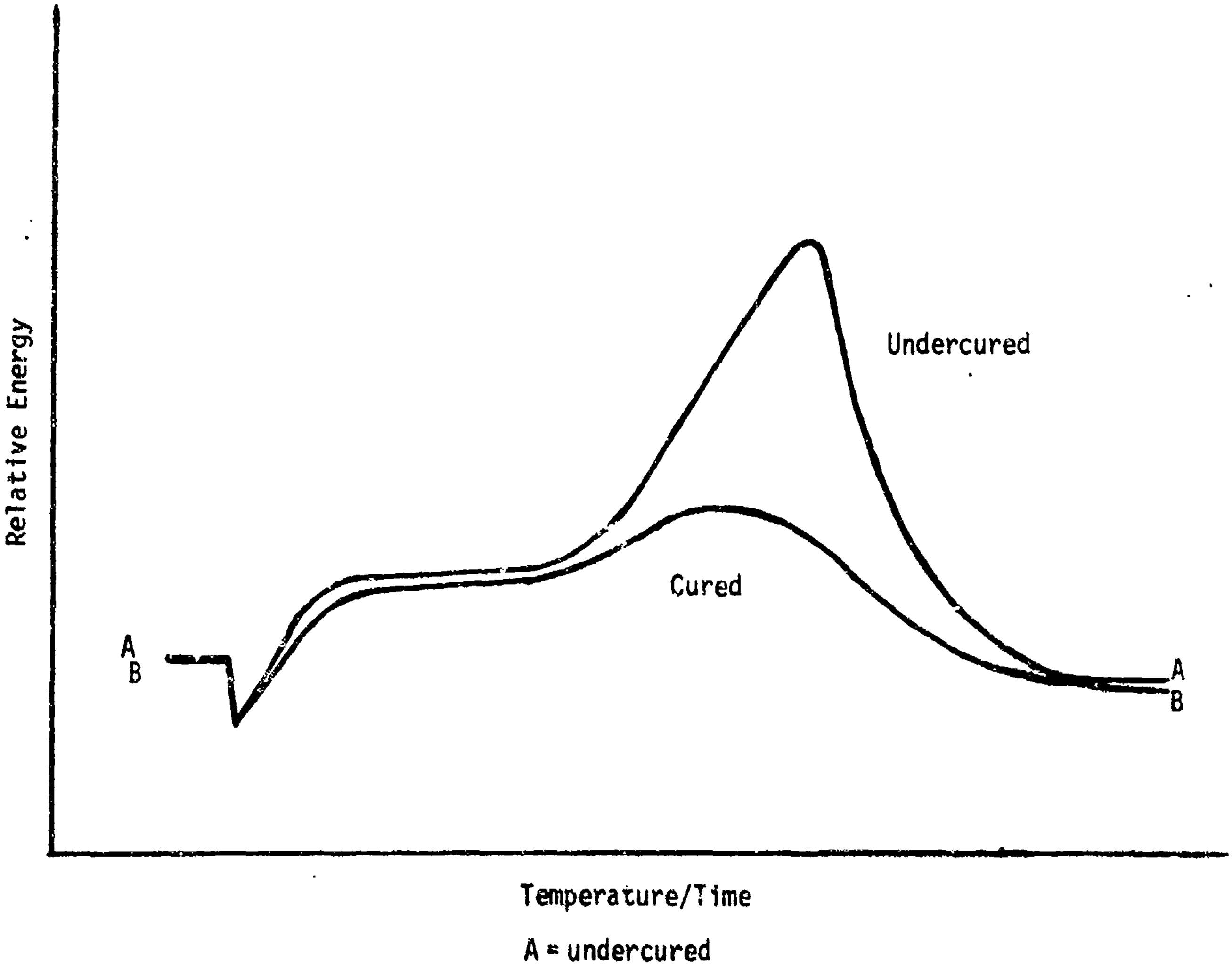


FIGURE 1. DSC EXAMPLE TRACE

Battelle used the following conditions listed in Table 2 to conduct the DSC tests.

TABLE 2. DSC OPERATING CONDITIONS

Temperature Scan Range	25-150 C
Heat Rate	10 C/min
Sample Size	15 mg
Flow Rate	30 cc/min
Sample Pan	Aluminum, covered
Atmosphere	Nitrogen

The DSC traces of the four samples:

- interior bow
- exterior bow
- interior stern
- exterior stern

are located in Appendix B, pages B-1 through B-12. Three replicates of each sample were run and are designated by an "A", "B", or "C" after each sample name and number.

DSC Results

In a typical DSC trace, a constant slope baseline would indicate a cured laminate system. Because this test is dynamic, it is not possible to determine analytically the extent of reaction of the "as received" laminates. It is only possible to say that in no case was a sample studied that was fully reacted. In the case of a two-stage cross-linked polyester resin, an ideal DSC experiment would yield a straight line with only a small deviation in slope at the glass transition point (Tg) prior to reaching degradation. If a sample has not been fully cured, however, a noticeable peak would occur corresponding to the energy needed to more fully cure the system. Such a peak was found in all 12 DSC's in the laminate samples. In Figures B-1 through B-12, the highest curve of the two curves in the figure represents the first heating of the chosen sample. The lower curve represents the same sample which had undergone heating from 25 to 150°C and then quenching to 25°C followed by reheating to 150°C. In all cases, peaks indicating an endothermal reaction were identified during the first and second runs, which are believed to be a continuation of the curing reaction. Because the area under the first curve is greater than that under the second curve, it is presumed that the mixture is becoming more fully cured after the initial heating.

Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) provides a quantitative measurement of any weight change associated with a transition. For example, a TGA can directly record the weight loss of a sample with respect to temperature or time, due to dehydration or decomposition. TGA curves are characteristic for a given compound or system because of the unique sequence of physico-chemical reactions which occur at definite temperature ranges and at rates that are a function of the molecular structure.

TGA is perhaps most useful when it complements the DSC analysis. Virtually all weight-change processes absorb or release energy and are thus measurable by DSC, but not all energy-change processes are accompanied by changes in weight. This difference in the two techniques enables a distinction to be made between physical and chemical changes when the samples are subjected to DSC and TGA tests.

A Cahn electrobalance with an associated F&M-200 Programmable heater was used to conduct the analysis. Table 3 indicates the TGA test conditions used in this program.

TABLE 3. TGA TEST CONDITIONS

Sample Size	50 mg
Temperature Range	20-900 C
Heat Rate	10°C/min
Atmosphere	Air

The samples were prepared as described in the sample preparation section, and the thermograms are located in Appendix B, pages B-13 through B-17.

TGA Testing Results

Direct evidence for non-homogeneity is evident in TGA data. The weight loss versus temperature traces in the TGA experiment (Appendix, pages B-13 through B-17) show several apparent differences. The most apparent of these is that the glass fiber content of the gel coat side varies by at least 20% (from 25% glass in the bow gel coat layer to 30% glass in the stern gel coat layer). Even taking into account the different thicknesses of the sections, this large absolute difference certainly suggests that it is possible to have significant quantities of poorly dispersed glass fiber.

A second observation from the TGA results is that the measured low-temperature volatiles, assumed to be water, varied considerably depending on sample location on the boat and sample depth from the exterior surface. The interior samples from both the bow and stern showed essentially no water. This was expected since these samples were held at 72 F and 50% R.H. for 2 weeks prior to testing. However, the gel coat sides of both samples showed measurable quantities of water present (up to 0.3%).

Thermomechanical Analysis

Thermomechanical Analysis (TMA) provides a measurement of penetration, expansion, contraction, and extension of a material as a function of temperature. One of the common applications of this test is to determine the homogeneity of a sample. Since the expansion, contraction, penetration, and extension of a material are characteristic of composition, then differences in the thermograms indicate different compositions.

A Perkin-Elmer TMS Thermomechanical Analyzer was used to perform this task. The TMA operating conditions for this test are described in the table below.

TABLE 4. TMA OPERATING CONDITIONS

Sample Size:	50 mg
Probe:	Penetration
Atmosphere:	Helium
Heat Rate:	10°C/min
Pressure:	7 psi
Flow Rate	30 cm^3/min
Temperature Scan:	0-250°C

A sample was prepared as previously described in the "Sample Preparation Section". A sample was then placed in the sample holder and the probe lowered until it just touched the surface of the sample. The temperature of the sample was increased at a rate of 10°C/min and the displacement of the probe was monitored using a linear variable differential transformer detector attached to an X-Y recorder. Copies of these recordings may be found in Appendix B pages B-13 through B-16.

TMA Results

The TMA results support the contention that the samples are not homogeneous in nature. The most important difference between the bow samples and the stern samples (both external and gel coat sides), is that the bow samples show a significant penetration at 60^{o}C followed by expansion of the glass-filled matrix. One expected cause for such behavior would be that the probe was resting on the cured polyester resin surface and, upon heating, softens the surface and penetrates until contacting the much stiffer fiber matrix which was expanding with the rising temperature. The stern samples did not show the initial penetration, indicative of a resin-rich surface, but instead showed only an expansion after 60^{o}C. This behavior could be interpreted as the presence of glass fiber at or near the surface of the sample. The closer that the glass is to the surface of the material, the easier it is for water to penetrate into the matrix.

The unhomogeneities discovered in these two sample tests indicate variability in fabrication control. As a result of the variability, it is likely that problems in structural integrity of the laminate could result.

Gel Permeation Chromotography

Gel permeation chromotography (GPC) is a non-interactive method of molecular separation, providing a method to determine the molecular weight distribution of a sample. This test will, therefore, give an indication of significant cure. Ideally, a 100% cured system will yield no extractable material but, realistically, no system can ever eliminate all low-molecular weight materials. however, this method is valid for materials with molecular weights in the thousands.

A Waters Model 150C ALC/GPC gel permeation chromatograph was used to determine the approximate molecular weight of the extractable polyester from the composite laminate. Each of the four samples were extracted for one week in 150 milliliters of chloroform, then filtered and injected into the GPC column. The operating conditions for this analysis are listed in Table 5.

TABLE 5. GPC OPERATING CONDITIONS

Solvent:	chloroform
Flow rate:	1 mL/min
Temperature:	23°C
Sample concentration:	2 mg/mL
Injection Volume:	100 µL
Columns:	10^4-10^3-500-100 A µ Styragel

The molecular weights reported are not absolute but are relative to a polystyrene calibration curve for the given conditions. The GPC chromatograms can be found in Appendix B page B-21.

GPC Results

The GPC chromatograms indicate a low molecular weight species, as evidenced by the late eluting species between 42 and 45 minutes. There are also high molecular weight materials eluting at 31 minutes, peaking at 35 minutes, and ultimately running into the low molecular weight peaks at 42 minutes. In a fully reacted system, none of the peaks would be expected except the two low molecular weight at 42 minutes. The peak at 35 is probably unreacted oligomer.

APPENDIX A

REPAIR

APPENDIX A

REPAIR

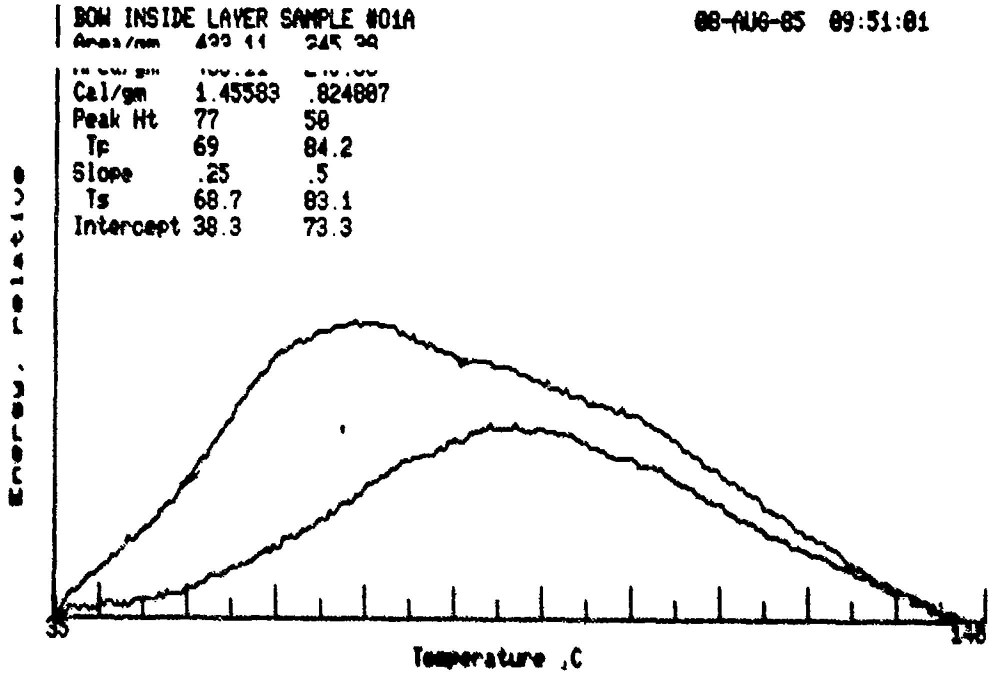
Many attempts have been made to develop a means of repairing blistered hulls.(22,25) The best of these yielded about an 80% success rate. The recommended procedure is as follows:

- Carefully dry-grind the gel coat away over the defective areas down to the laminate.
- Use a high-pressure freshwater spray to remove salts and contaminants from the glass fibers.
- The boat should be placed in a warm, dry, well- ventilated place to dry out. This may take some time, depending on the amount of water absorbed.
- When the laminate is absolutely dry, it should be covered with a couple of coats of two-pack epoxy or two-pack polyurethane paint, being careful not to trap any air bubbles.
- A solventless epoxy filler should be applied to fill any pits and cover the laminate with a thickness of at least 0.6 mm to cover all fibers and thereby prevent wicking.
- Four coats of two-pack epoxy or two-pack polyurethane paint should be applied.

One filler which has been tested for this type of application is AF-163-2 from 3M. AS/3501-6 graphite epoxy reportedly works well also.

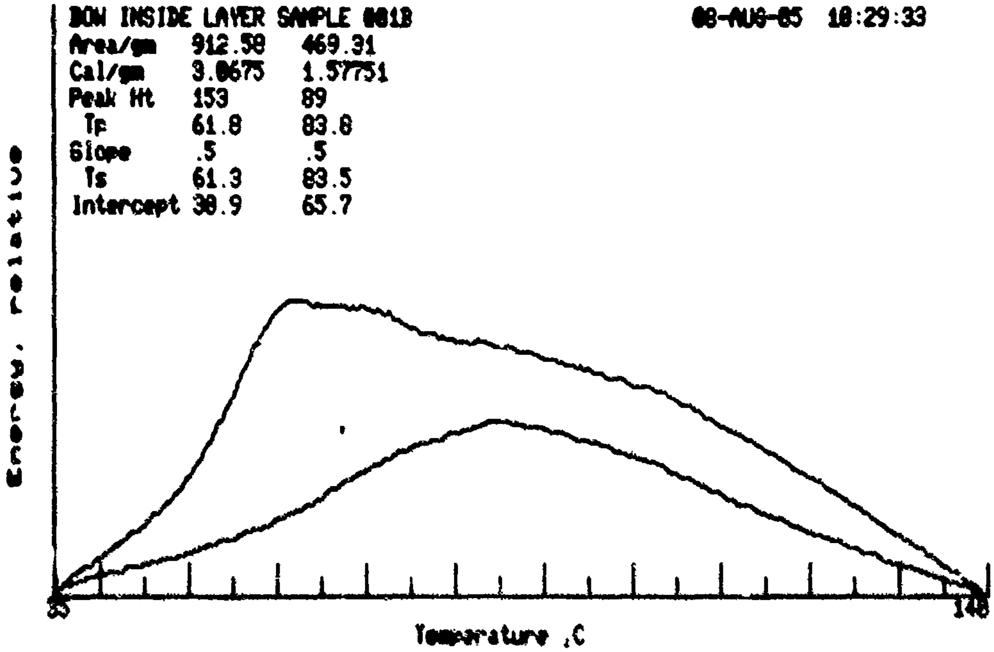
APPENDIX B

SAMPLE ANALYSIS DATA



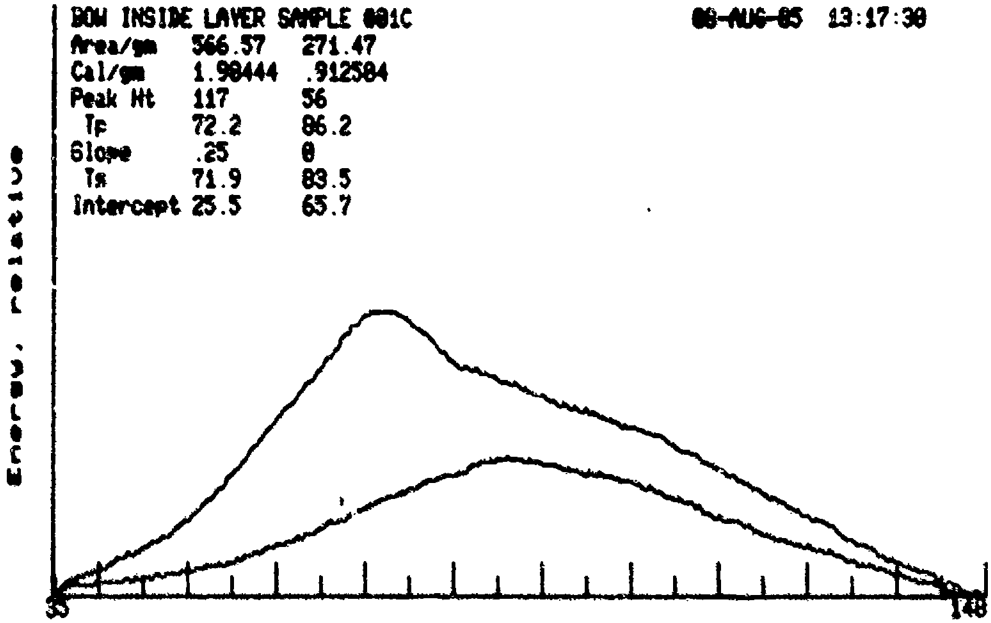
```
BOW INSIDE LAYER SAMPLE #01A                          08-AUG-85  09:51:01
Area/gm     433.11   245.38
[illegible]
Cal/gm      1.45583  .824807
Peak Ht     77       58
 Tp         69       84.2
Slope       .25      .5
 Ts         68.7     83.1
Intercept   38.3     73.3
```

FIGURE B-1. DSC TRACE: BOW INTERNAL LAYER SAMPLE A



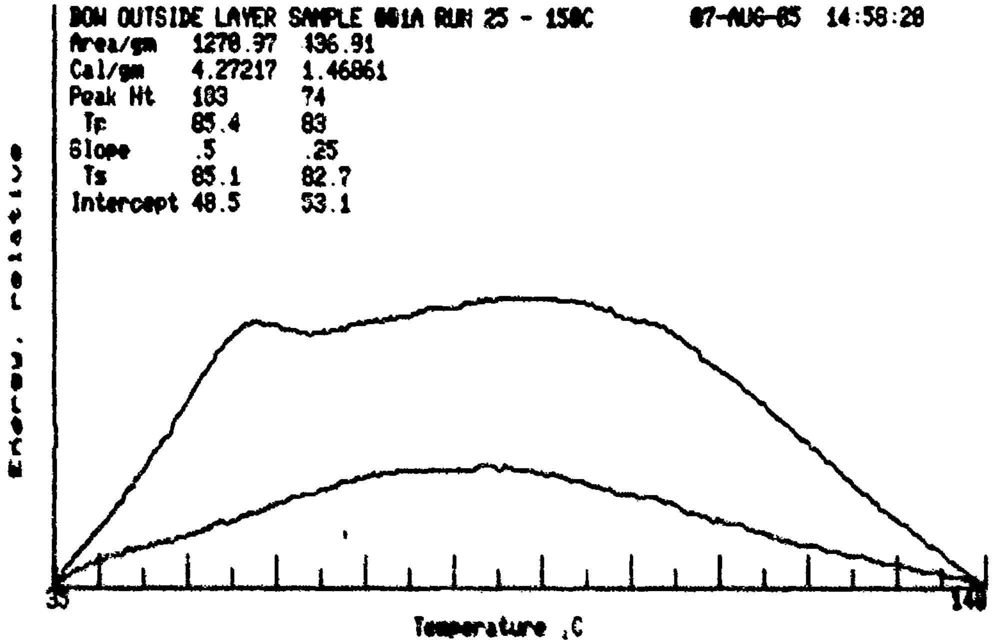
```
BOW INSIDE LAYER SAMPLE 001B                              08-AUG-85  10:29:33
Area/gm    912.50    469.31
Cal/gm     3.0675    1.57751
Peak Ht    153       89
 Tp        61.0      83.0
Slope      .5        .5
 Ts        61.3      83.5
Intercept  30.9      65.7
```

FIGURE B-2. DSC TRACE: BOW INTERNAL LAYER SAMPLE B



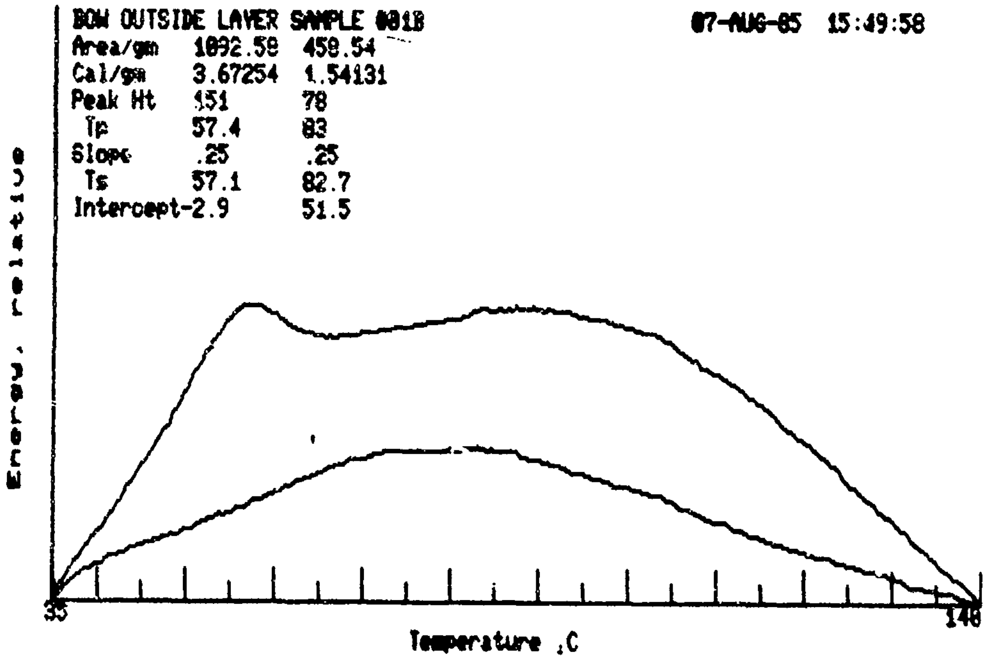
```
BOW INSIDE LAYER SAMPLE 001C                         08-AUG-85  13:17:38
Area/gm    566.57   271.47
Cal/gm     1.98444  .912584
Peak Ht    117      56
 Tp        72.2     86.2
Slope      .25      0
 Ts        71.9     83.5
Intercept  25.5     65.7
```

FIGURE B-3. DSC TRACE: BOW INTERNAL LAYER SAMPLE C



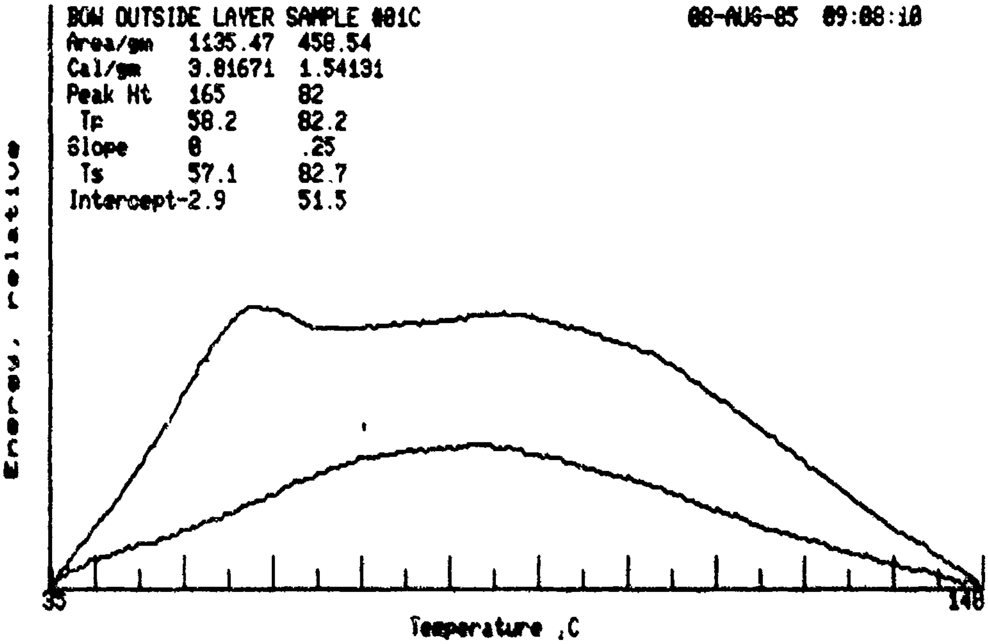
```
BOW OUTSIDE LAYER SAMPLE 001A RUN 25 - 150C        07-AUG-85  14:58:20
Area/gm    1270.97  136.91
Cal/gm     4.27217  1.46861
Peak Ht    103      74
 Tp        85.4     83
Slope       .5       .25
 Ts        85.1     82.7
Intercept  48.5     53.1
```

FIGURE B-4. DSC TRACE: BOW EXTERNAL LAYER SAMPLE A



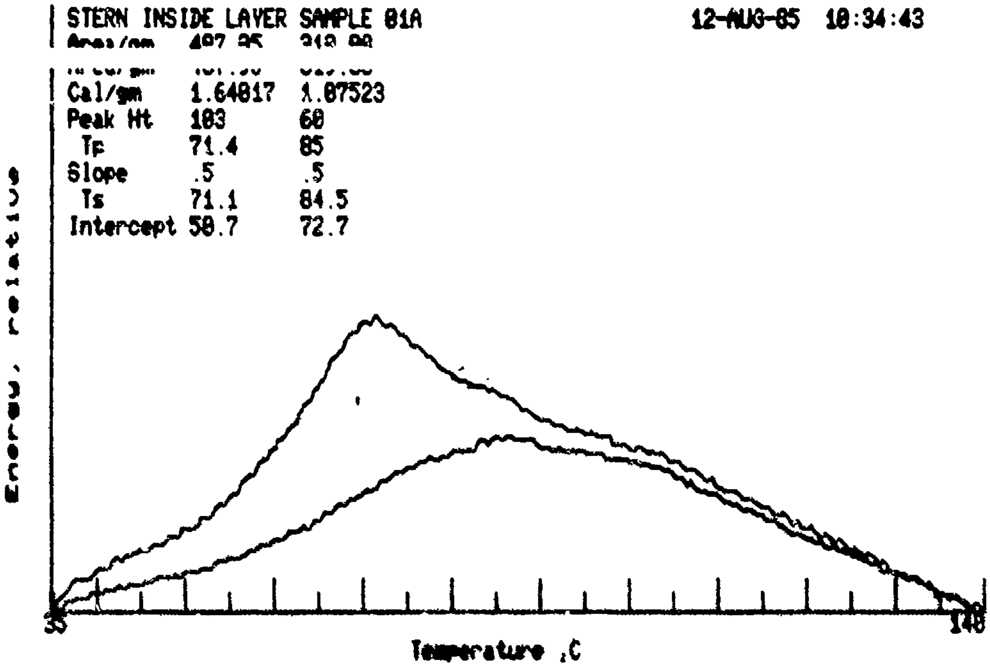
```
BOW OUTSIDE LAYER SAMPLE 001B                          07-AUG-85  15:49:58
Area/gm    1092.58  458.54
Cal/gm     3.67254  1.54131
Peak Ht    151      78
 Tp        57.4     83
Slope      .25      .25
 Ts        57.1     82.7
Intercept-2.9       51.5
```

FIGURE B-5. DSC TRACE: BOW EXTERNAL LAYER
SAMPLE B



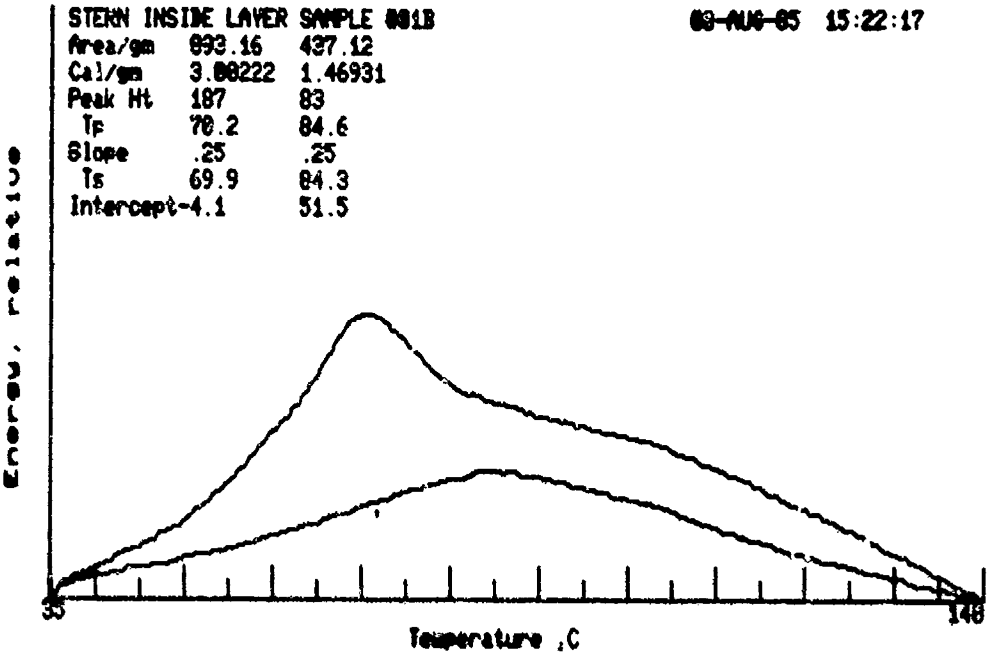
```
BOW OUTSIDE LAYER SAMPLE #01C                        08-AUG-85  09:08:10
Area/gm     1135.47  458.54
Cal/gm      3.01671  1.54131
Peak Ht     165      82
 Tp         58.2     82.2
Slope       0        .25
 Ts         57.1     82.7
Intercept-2.9        51.5
```

FIGURE B-6. DSC TRACE: BOW EXTERNAL LAYER
SAMPLE C



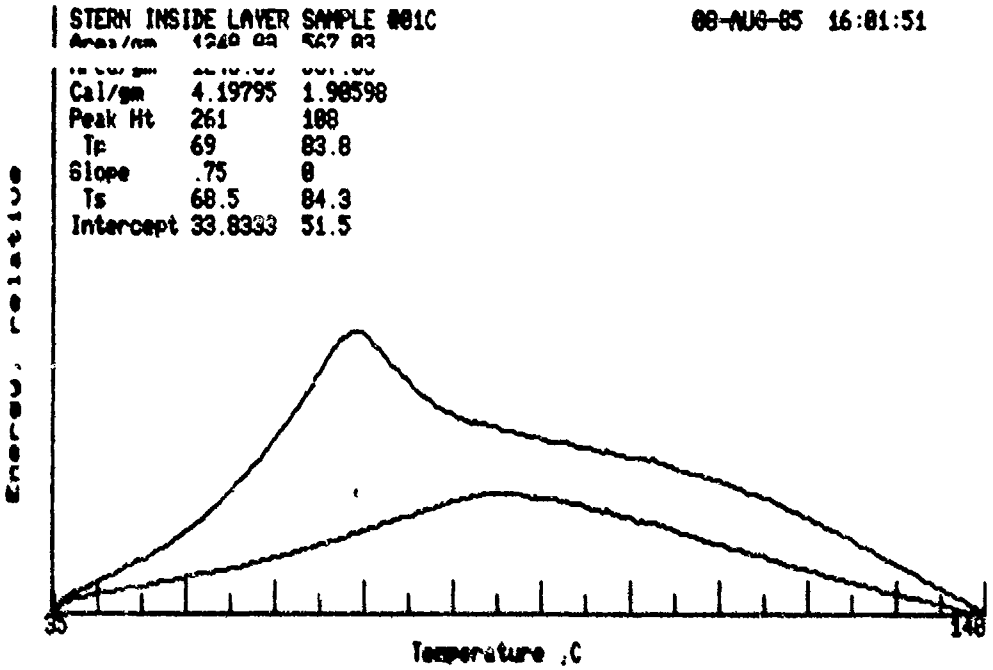
```
STERN INSIDE LAYER SAMPLE 01A                     12-AUG-85  10:34:43
Area/gm    [illegible]  [illegible]
[illegible]
Cal/gm     1.64017  1.07523
Peak Ht    103      60
 Tp        71.4     85
Slope      .5       .5
 Ts        71.1     84.5
Intercept  50.7     72.7
```

FIGURE B-7. DSC TRACE: STERN INTERNAL LAYER SAMPLE A



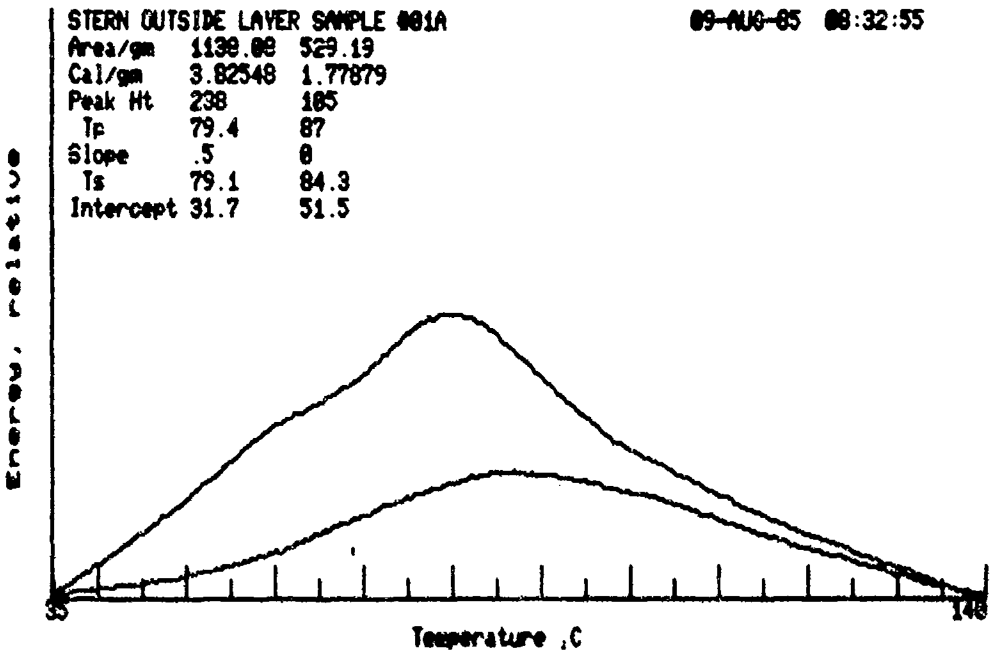
```
STERN INSIDE LAYER SAMPLE 001B                  09-AUG-85  15:22:17
Area/gm    893.16    437.12
Cal/gm     3.00222   1.46931
Peak Ht    187       83
  Tp       70.2      84.6
Slope      .25       .25
  Ts       69.9      84.3
Intercept-4.1        51.5
```

FIGURE B-8. DSC TRACE: STERN INTERNAL LAYER
SAMPLE B



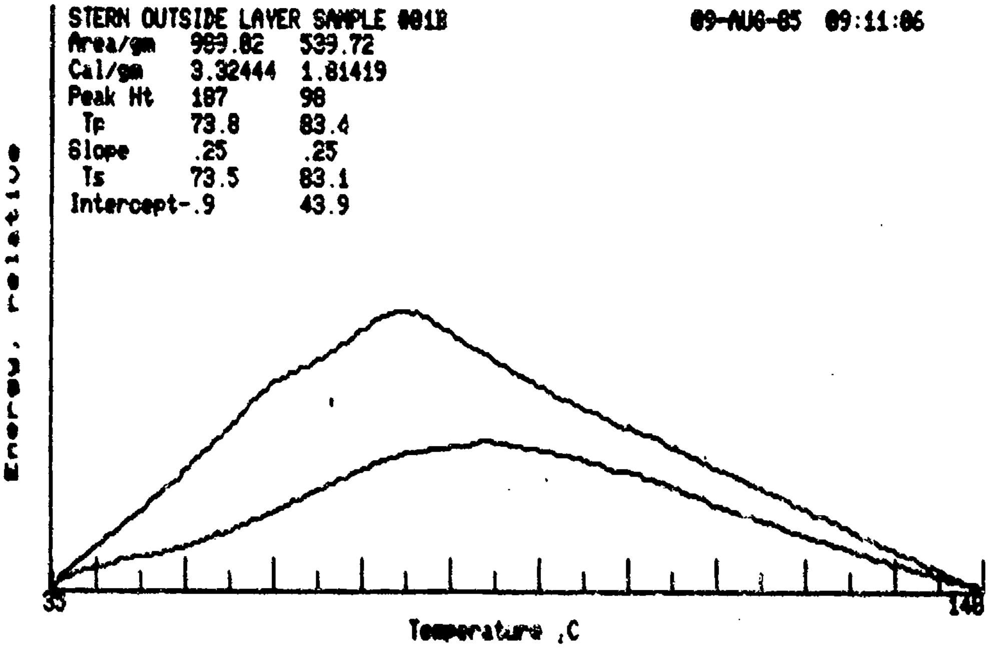
```
STERN INSIDE LAYER SAMPLE #01C                    08-AUG-85  16:01:51
Area/gm     1249.93  567.93
[illegible]
Cal/gm      4.19795  1.90598
Peak Ht     261      108
 Tp         69       83.8
Slope       .75      0
 Ts         68.5     84.3
Intercept   33.8333  51.5
```

FIGURE B-9. DSC TRACE: STERN INTERNAL LAYER SAMPLE C



```
STERN OUTSIDE LAYER SAMPLE 001A                        09-AUG-85  08:32:55
Area/gm    1130.00  529.19
Cal/gm     3.82548  1.77879
Peak Ht    238      105
 Tp        79.4     87
Slope      .5       0
 Ts        79.1     84.3
Intercept 31.7      51.5
```

FIGURE B-10. DSC TRACE: STERN EXTERNAL LAYER SAMPLE A



```
STERN OUTSIDE LAYER SAMPLE #01B                       09-AUG-85  09:11:06
Area/gm    989.02   539.72
Cal/gm     3.32444  1.81419
Peak Ht    187      98
 Tp        73.8     83.4
Slope      .25      .25
 Ts        73.5     83.1
Intercept-.9        43.9
```

FIGURE B-11. DSC TRACE: STERN EXTERNAL LAYER SAMPLE B

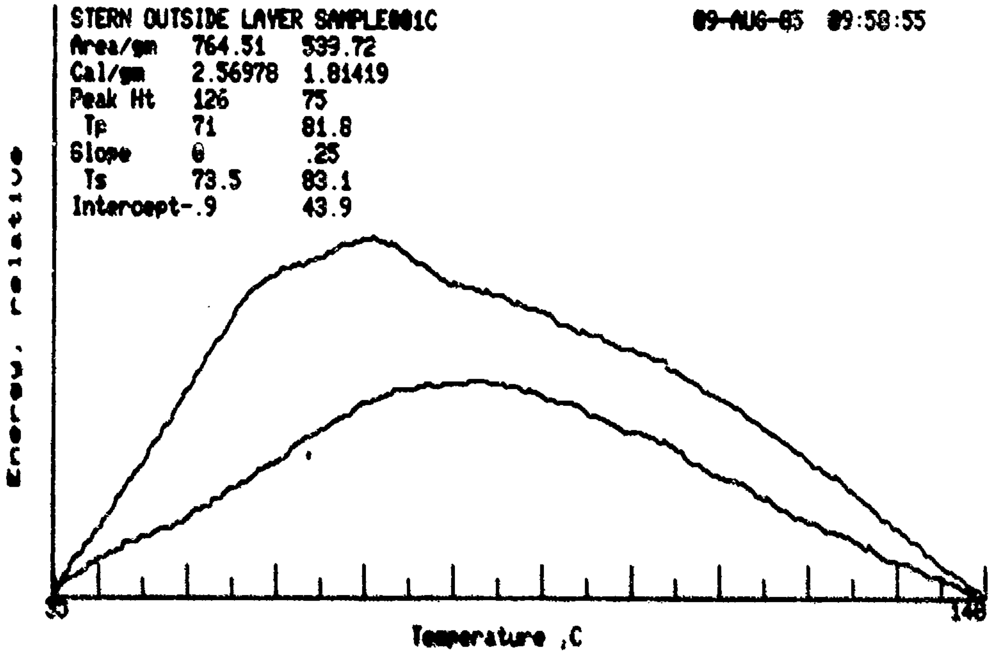


FIGURE B-12. DSC TRACE: STERN EXTERNAL LAYER
<u>SAMPLE C</u>

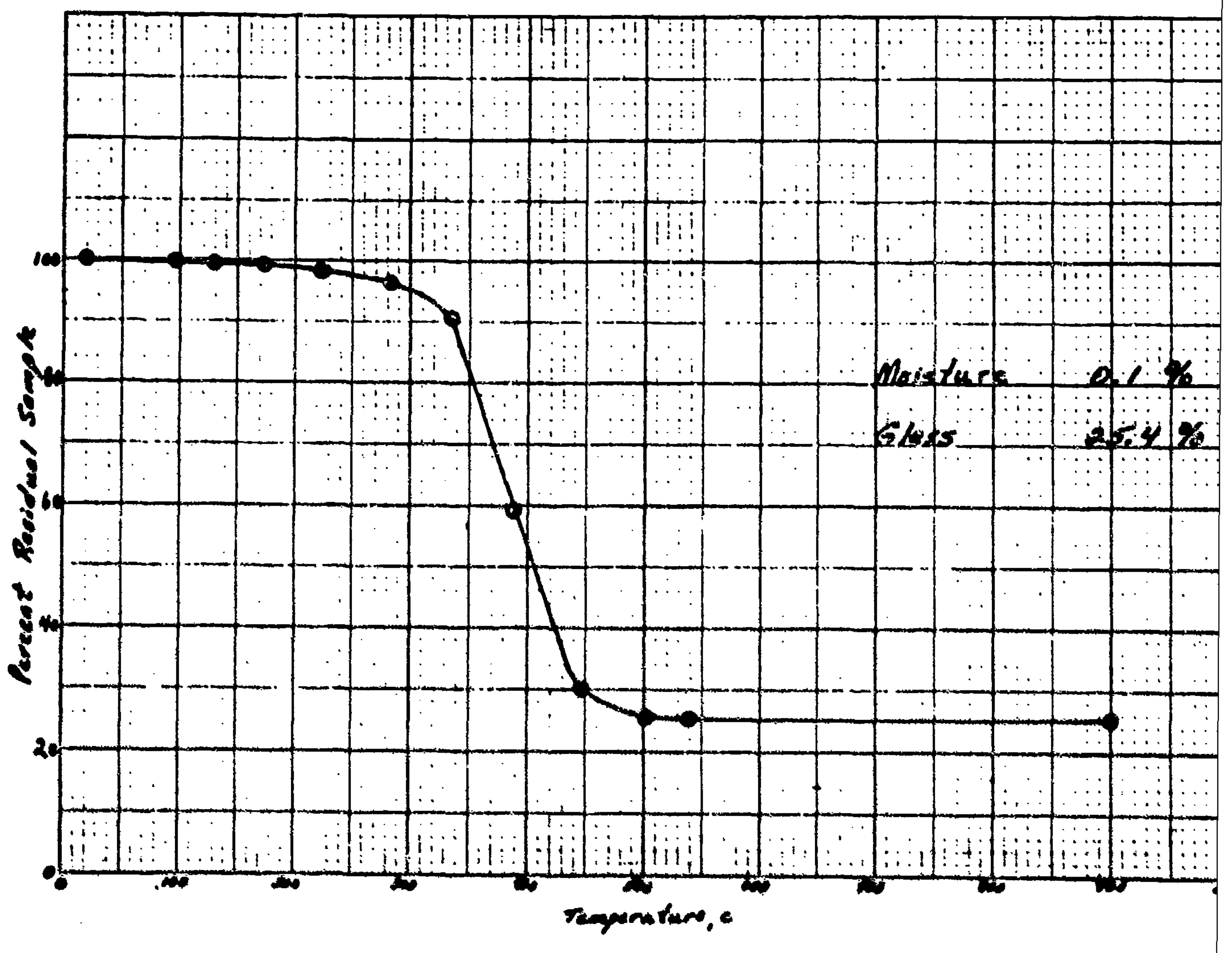


FIGURE B-13. THERMOGRAM OF BOW (EXTERNAL) AT 10 c/min HEATING RATE IN AIR

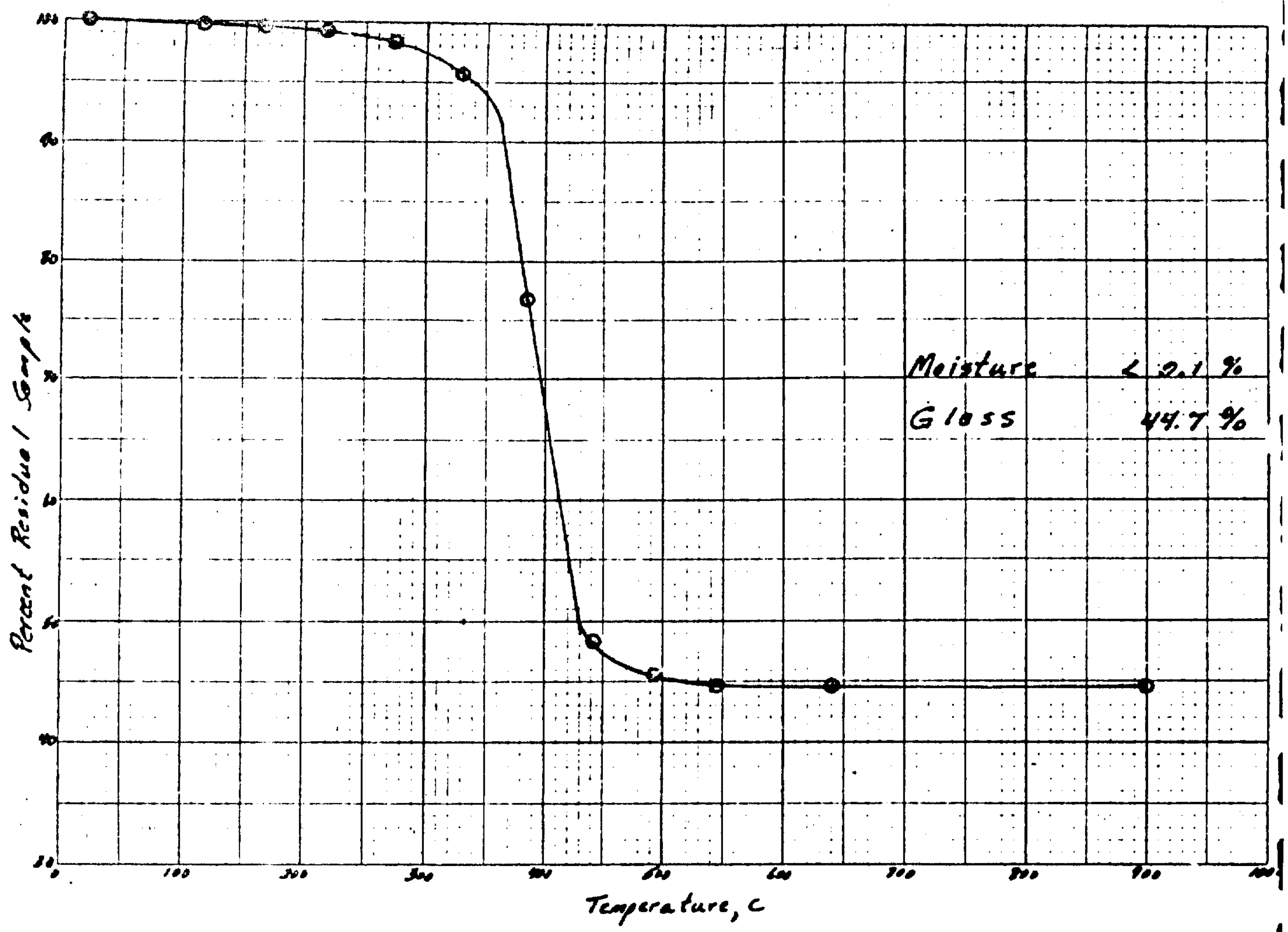


FIGURE B-14. THERMOGRAM OF BOW (INTERNAL) AT 10 c/min HEATING RATE IN AIR

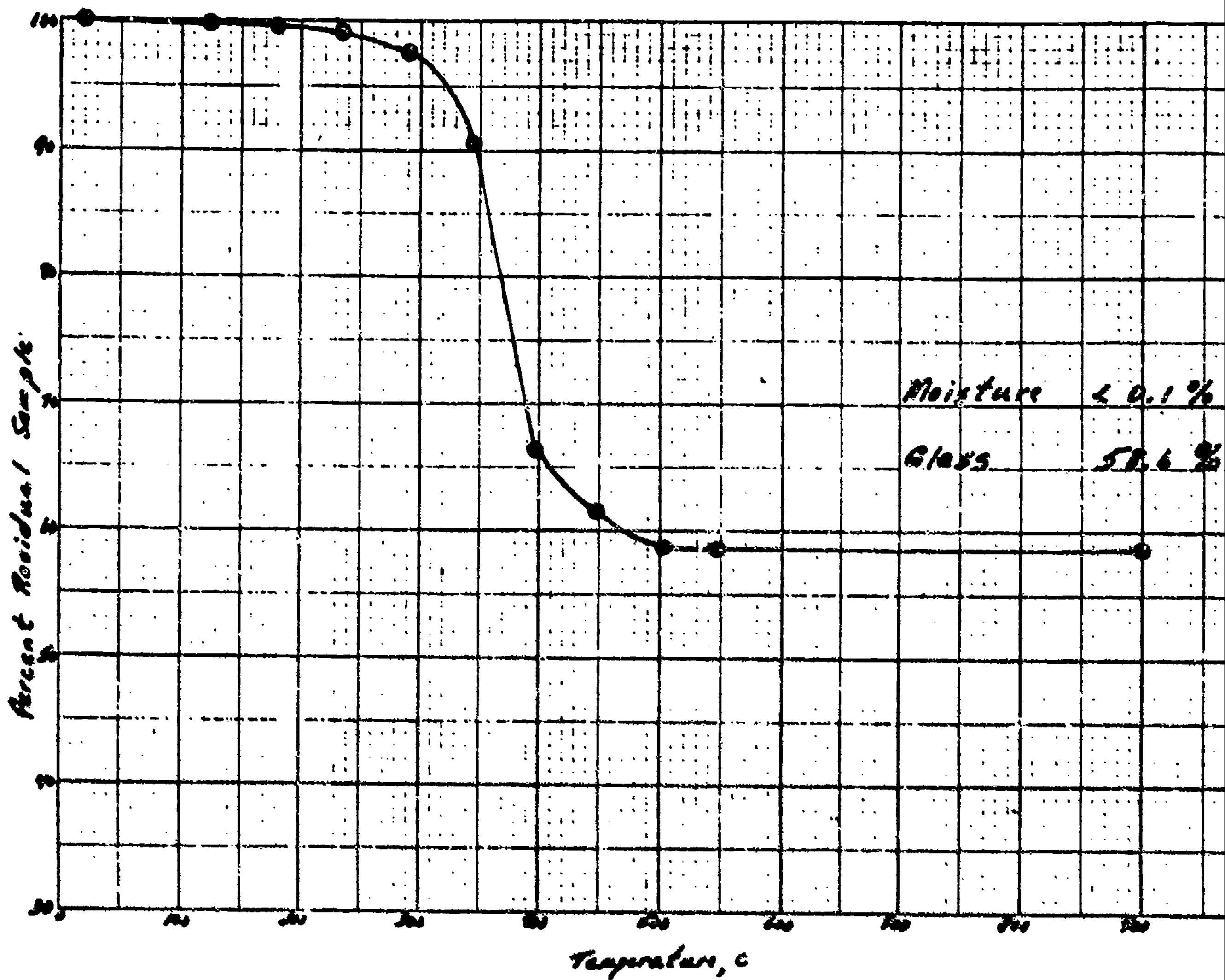


FIGURE B-15. THERMOGRAM OF STERN (INTERNAL) AT 10 c/min HEATING RATE IN AIR

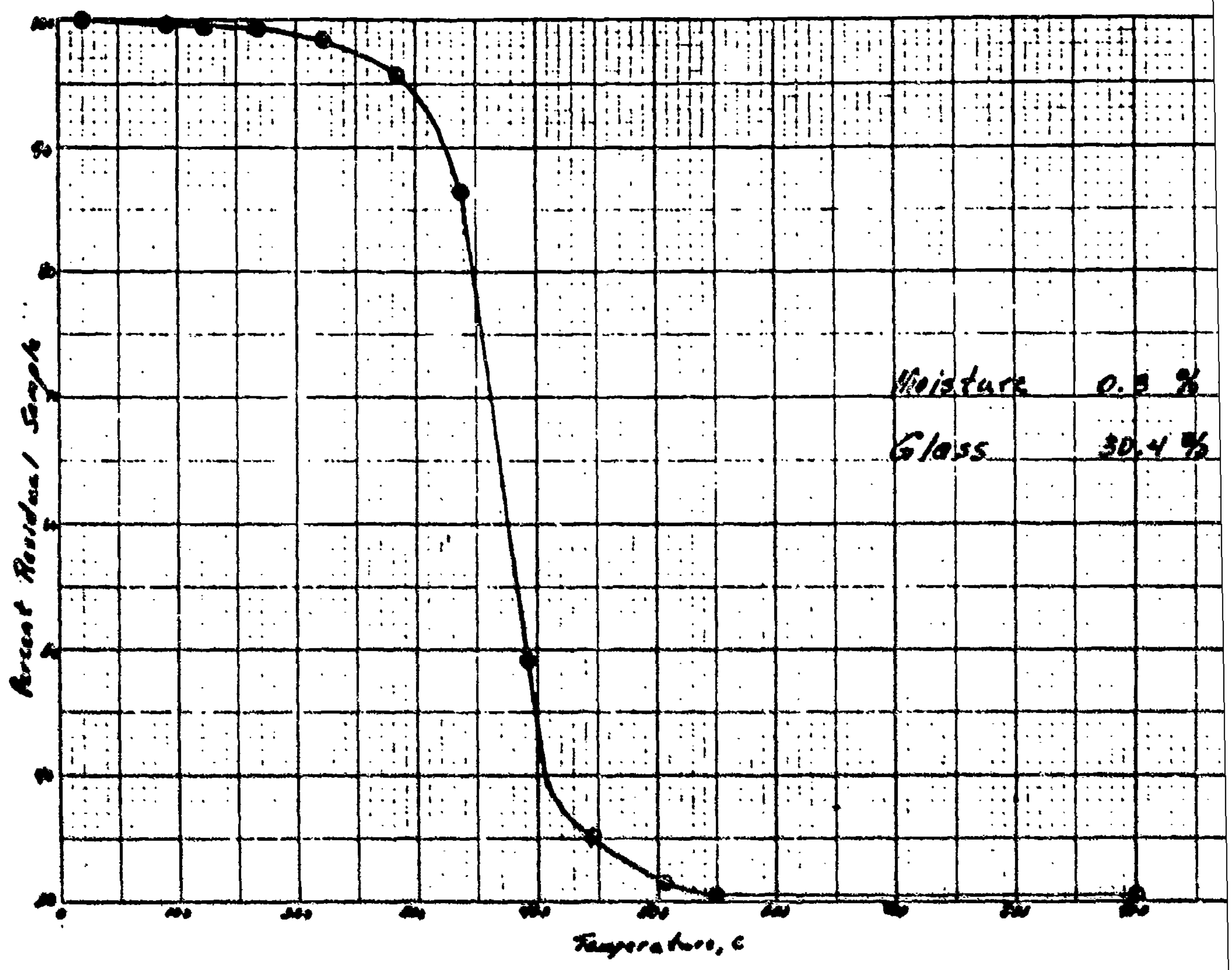
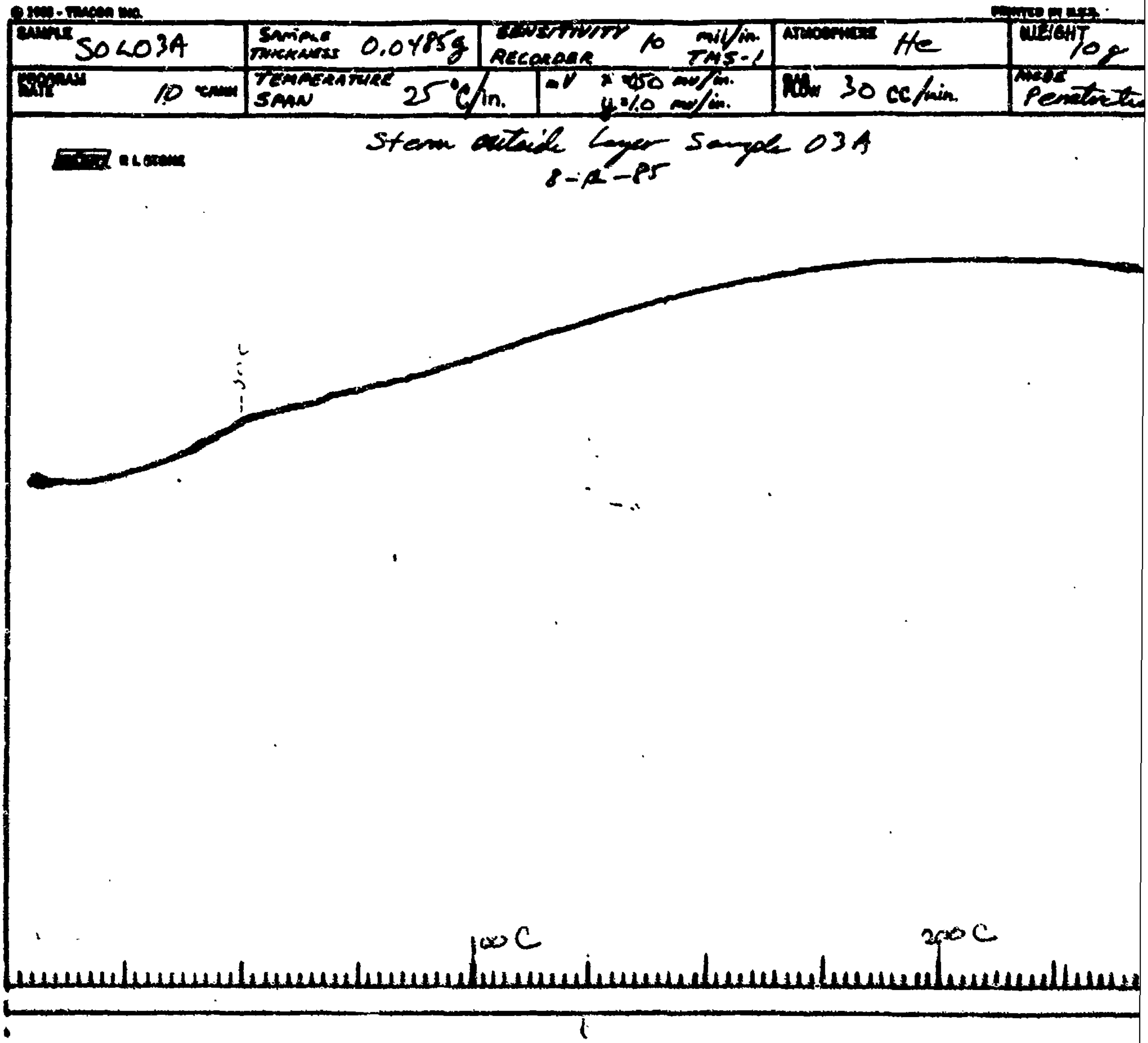


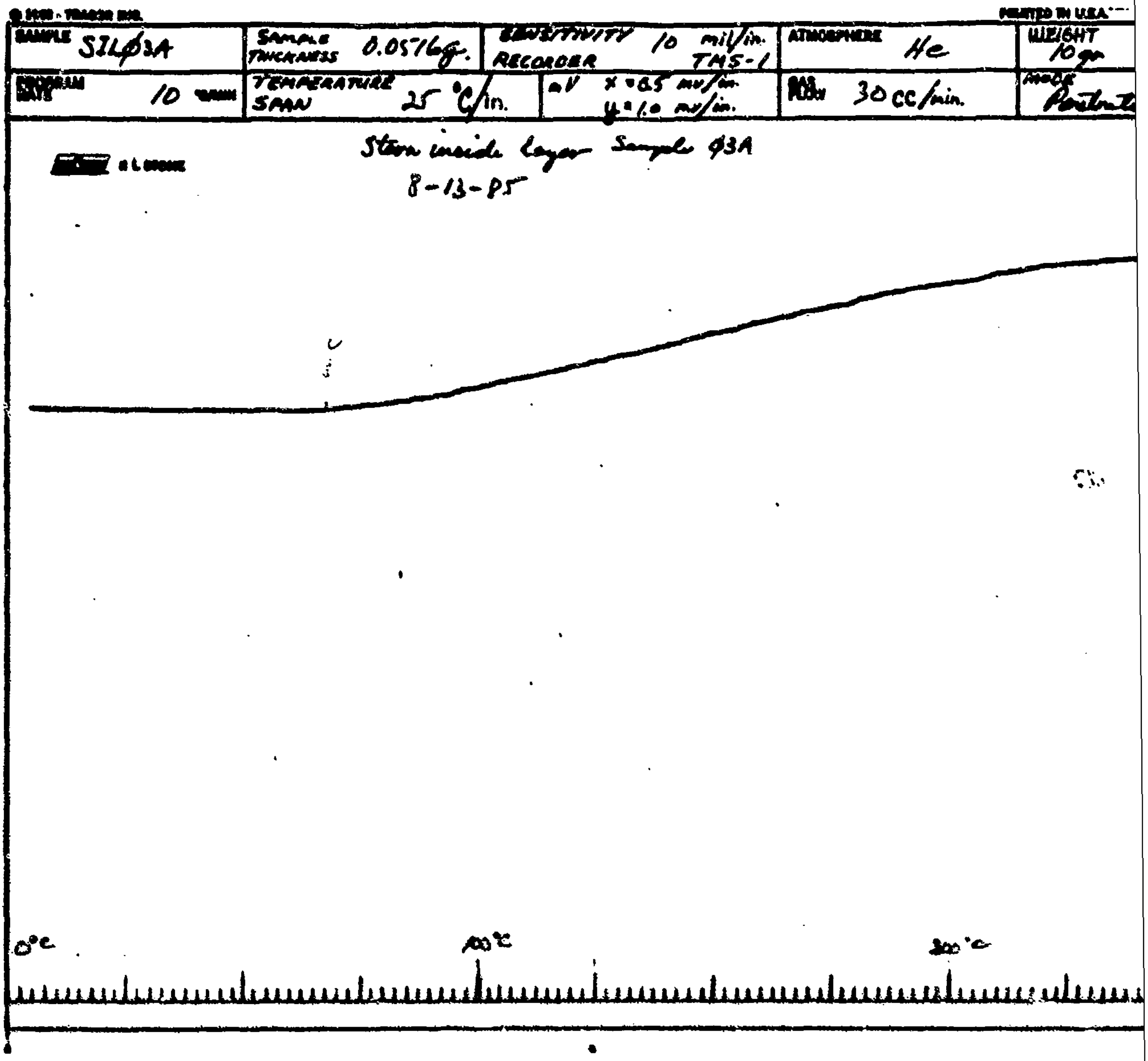
FIGURE B-16. THERMOGRAM OF STERN (EXTERNAL) AT 10 c/min HEATING RATE IN AIR



SAMPLE SO LO3A	SAMPLE THICKNESS 0.0485g	SENSITIVITY 10 mil/in. RECORDER TMS-1	ATMOSPHERE He	WEIGHT 10 g
PROGRAM RATE 10 °C/MIN	TEMPERATURE SPAN 25°C/in.	mV x = 50 mv/in. y = 1.0 mv/in.	GAS FLOW 30 cc/min.	MODE Penetrati

Stern outside Layer Sample 03A
8-12-85

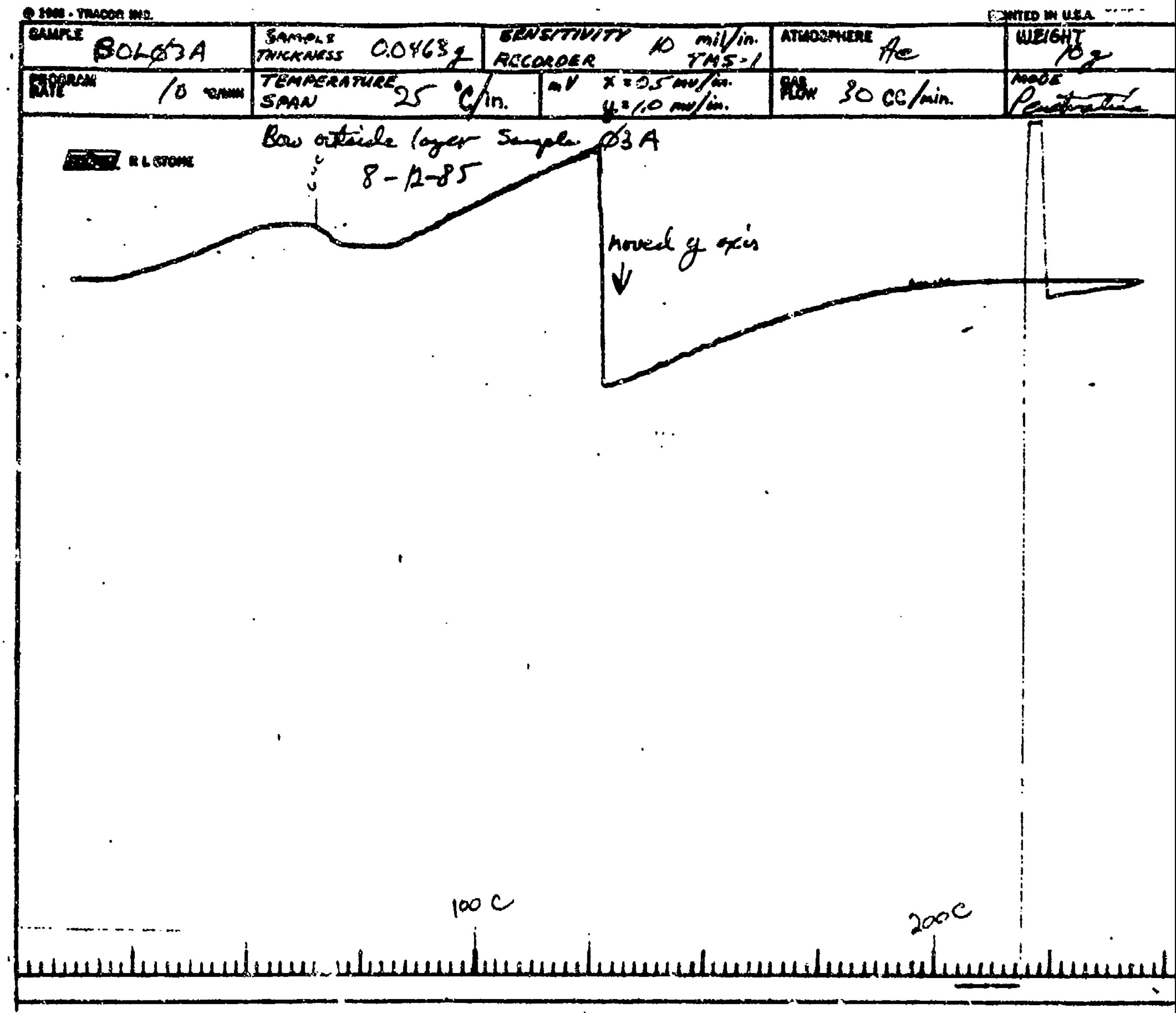
FIGURE B-17. TMA ANALYSIS OF STERN (INTERNAL) SAMPLE A



SAMPLE SIL03A	SAMPLE THICKNESS 0.0516g.	SENSITIVITY 10 mil/in. RECORDER TMS-1	ATMOSPHERE He	WEIGHT 10 gm
PROGRAM RATE 10 °/MIN	TEMPERATURE SPAN 25 °C/in.	mV x = 0.5 mv/in. y = 1.0 mv/in.	GAS FLOW 30 cc/min.	MODE

Stern inside layer Sample 03A
8-13-85

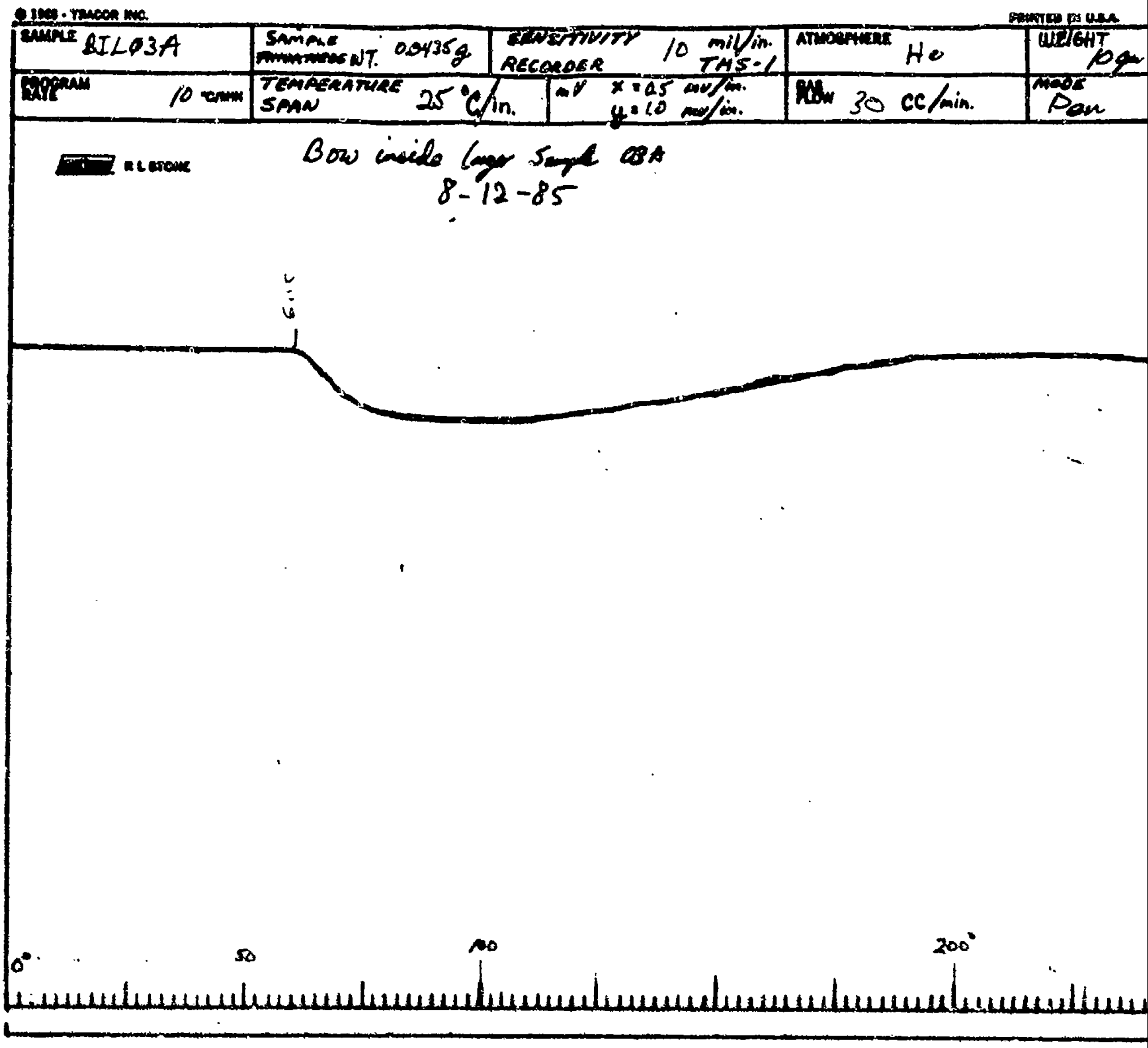
FIGURE B-18. TMA ANALYSIS OF BOW (EXTERNAL) LAYER SAMPLE A



SAMPLE BOL03A	SAMPLE THICKNESS 0.0463 g	SENSITIVITY 10 mil/in. RECORDER TMS-1	ATMOSPHERE He	WEIGHT 10 g
PROGRAM RATE 10 °C/MIN	TEMPERATURE SPAN 25 °C/in.	mV x = 0.5 mV/in. y = 1.0 mV/in.	GAS FLOW 30 cc/min.	MODE Penetration

Bow outside layer Sample 03A
8-12-85

FIGURE B-19. TMA ANALYSIS OF BOW (EXTERNAL) LAYER SAMPLE A



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SAMPLE BIL03A	SAMPLE ~~THICKNESS~~ WT. 0.0435 g	SENSITIVITY 10 mil/in. RECORDER TMS-1	ATMOSPHERE He	WEIGHT 10 mg
PROGRAM RATE 10 °C/min	TEMPERATURE SPAN 25 °C/in.	mV x = 0.5 mV/in. y = 1.0 mV/in.	GAS FLOW 30 cc/min.	MODE Pan

Bow inside layer Sample 03A
8-12-85

FIGURE B-20. TMA ANALYSIS OF BOW (INTERNAL) LAYER SAMPLE A

8-15-85

Bow inside layer

2.5082 g total solids

filtered + diluted 50%

in $CHCl_3$

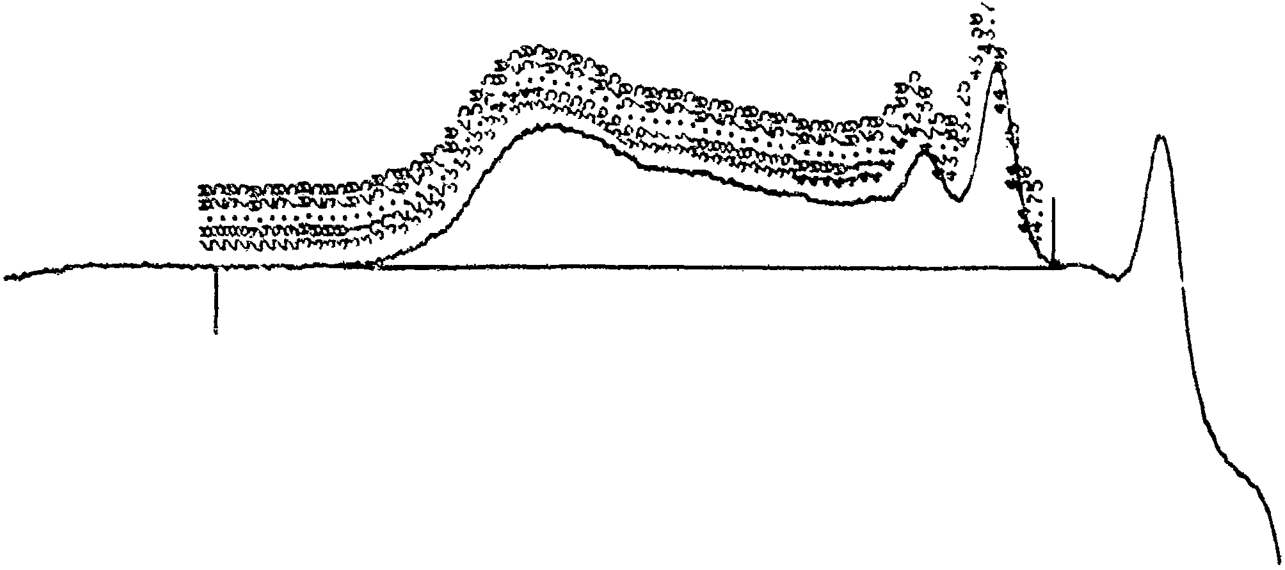

FIGURE B-21. GPC CHROMATOGRAMS ANALYSIS OF BOW (INTERNAL) LAYER

APPENDIX C

LITERATURE

"Osmosis in Resins and Laminates"
"Osmosis: Cause and Effect"
"Blister Performance of GRP Systems in Aqueous Environments"
"Blister Formation in RP: The Origin of the Osmotic Process"

Review of [illegible] history
and theories –
Note:- production
of glass fiber & fillers can
influence osmotic blistering if
hygroscopic element k are introduced

1984

Chapter 3

OSMOSIS IN RESINS AND LAMINATES

J. S. GHOTRA and G. PRITCHARD

School of Chemical and Physical Sciences, Kingston Polytechnic, Surrey, UK

SUMMARY

The principles of osmosis are familiar to students of physical chemistry. In recent years it has become apparent that osmotic pressure plays a part in many of the degradation processes observed during the exposure of crosslinked resins and fibre–resin composites to water. This chapter considers three of the processes, namely (1) resin matrix microcracking, (2) gelcoat blistering, and (3) (more briefly) fibre–resin debonding. The precise nature of the solutes contributing to osmotic pressure generation is considered, and the available evidence from chemical analysis is summarised. The advantages of using resins, fibres and additives which are inert to water, as far as is practicable, are clear.

3.1. INTRODUCTION

It has long been known that if there is a semi-permeable barrier dividing solvent from solution, there is a tendency for solvent to pass through the barrier wall into the solution, thus diluting it (Fig. 3.1). The flow of solvent is resisted by an osmotic pressure, a phenomenon investigated by many well-known workers in the field of dilute solutions, notably van't Hoff.[1,2] Many demonstrations of the phenomenon of osmotic pressure are described in standard texts, and many attempts have been made to quantify such experiments so as to predict the

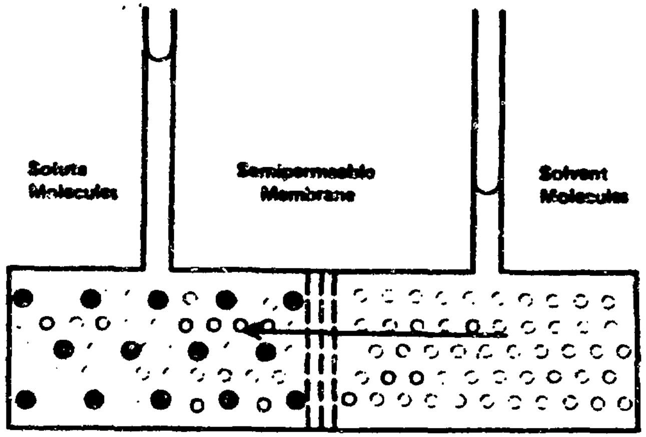

FIG. 3.1. Osmotic flow through a semi-permeable membrane.

magnitude of the osmotic pressures obtained under given circumstances.

C-1

The term 'semi-permeable' is intended here to mean that the barrier or membrane is permeable to solvent but not to solute. The actual magnitude of the permeability coefficient with respect to solvent is of secondary importance. Early investigators used animal membranes, which were not strictly semi-permeable since they allowed some transport by the solute. Subsequent experiments led to the development of artificial membranes of copper ferrocyanide, which were more satisfactory in this respect, and which were used in many quantitative experiments.

Studies of permeability data relating to organic crosslinked polymers such as unsaturated polyesters and epoxide resins indicate that in many instances these substances must be regarded as semi-permeable membranes, since they allow the passage of water relatively easily, whereas the rate of diffusion of large cations and anions, and still more noticeably of certain organic molecules, is much retarded. It would be inaccurate to describe these crosslinked polymers as completely semi-permeable, but the deviation from the ideal is small for many solutes. Table 3.1 shows some typical magnitudes for the rate of transport of water through resins.[3–9] The values have been normalised to constant thickness, as suggested by Otto *et al.*[6]

The magnitude of the osmotic pressure is dependent, loosely speak-

TABLE 3.1.
WATER TRANSMISSION THROUGH POLYMERS*

Polymer	Temperature (°C)	Water transmission rate (kg m^{-2} per day)	Reference
Isophthalic polyester	80	$38{\cdot}4\times10^{-4}$	4
Isophthalic polyester	50	$4{\cdot}8\times10^{-4}$	3
Vinyl ester	50	$5{\cdot}9\times10^{-4}$	5
PVDF	138	22×10^{-3}	6
Ethylene/ TFE copolymer	140	$9{\cdot}8\times10^{-3}$	6
Bisphenol polyester	100	$8{\cdot}6\times10^{-3}$	7
DGEBA epoxy (polyamide cured)	50	$1{\cdot}5\times10^{-4}$	8
Alkyd	20	$6{\cdot}7\times10^{-4}$	9
Chlorinated rubber	20	$2{\cdot}3\times10^{-4}$	9

* Transmission rate normalised to 10 mm thickness. PVDF, Polyvinylidene fluoride; TFE, tetrafluoroethylene; DGEBA, diglycidyl ether of Bisphenol A.

ing, on the concentration of the solution involved. For non-electrolytes, the relation between concentration and pressure is analogous to the ideal gas law, i.e.

$$\pi V = nRT \tag{1}$$

where π is the osmotic pressure, R is the gas constant, and n is the number of moles of solute dissolved in V dm^3 of solution at absolute temperature T. However, for electrolyte solutions such as brine, the osmotic pressure is a function of the ionic strength, I, of the solution:

$$I = \tfrac{1}{2}\sum C_i Z_i^2 \tag{2}$$

where C_i and Z_i are, respectively, the molality and valence of each ionic species. It follows that, whenever a resin or a composite is immersed in a solvent capable of diffusing into the material, then provided the material contains within it some soluble substances, especially if phase-separated, there is opportunity for osmotic pressure pockets to arise. The purpose of this chapter is to review the literature

concerning the phenomena which could be expected as a result. The next section enumerates the main possibilities.

3.2. POTENTIAL CONSEQUENCES OF OSMOTIC PRESSURE POCKETS

Unreinforced, cast resins, containing trapped solutes and immersed in a suitable solvent, may be expected to experience internal stresses at the sites of high solute concentration, and in some cases, these stresses may be sufficient to rupture the resin. The length of time before rupture occurs depends on the diffusivity of the solvent and hence on the temperature, on the geometry of the sample of resin, on the nature of the solute and its distribution within the resin. Disc cracking was probably known to the resin industry, if only as an empirical observation, long before it was first discussed in the scientific literature. The resulting disc cracks are discussed in section 3.3.

The same kind of effect may also be observed in laminates, insofar as the resin-rich regions may be subject to osmotic rupture under suitable circumstances. Another possibility is the formation of blisters under the surface of, or within the interior of, laminates as a result of distortion by excessive inflow of solvent. The process is a slow one at ambient temperatures, however, and most of the reported cases of blistering at ambient temperatures are in the hulls of polyester–glass boats which have been in water for long periods, i.e. years rather than weeks. The most common manifestation of this problem is the development of blisters between the gel-coat, which is separated from the water only by paint, and the backup laminate, as shown schematically in Fig. 3.2. Glass–polyester swimming pool liners and chemical process equipment have to withstand more demanding conditions, since the water temperature is generally higher than that faced by boat hull laminates. This does not necessarily lead to more severe blistering, since exposure to the water is often intermittent and, in any case, chemical process equipment in particular is usually fabricated to very high standards using some of the best materials available. Nevertheless some cases of osmotic pressure problems do arise from time to time. Specific examples are sometimes mentioned in the literature.

Another possible manifestation of osmotic pressure in composite materials is the initiation of fibre–resin debonding by the development of pressure pockets at the surface of fibres, following the diffusion of

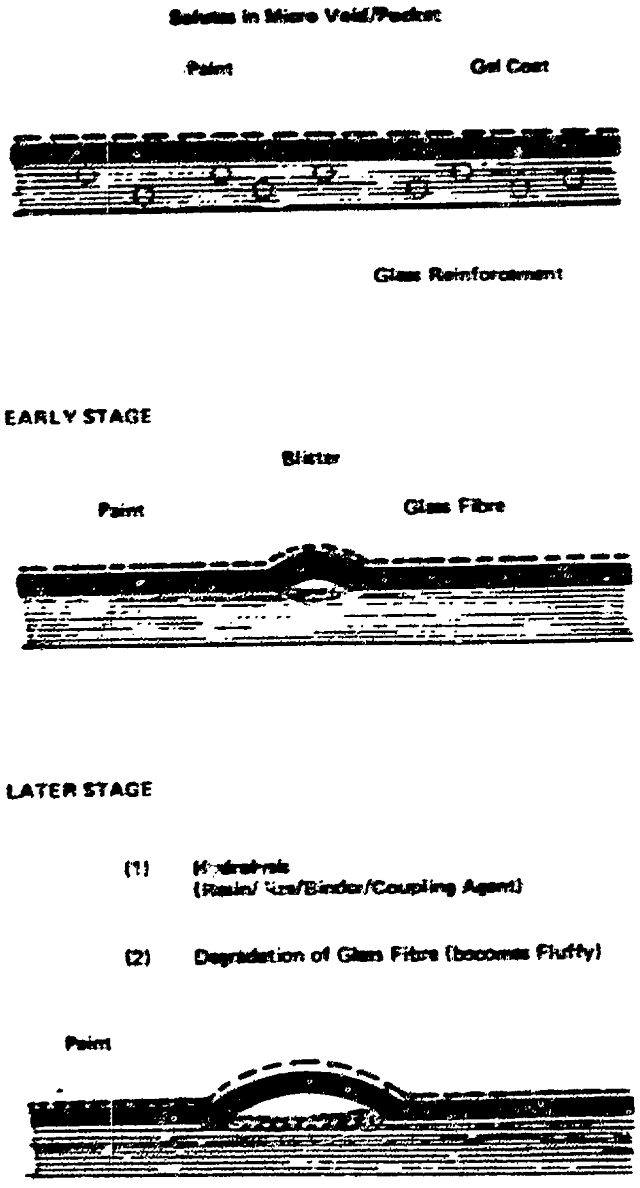

FIG. 3.2. Schematic illustration of gelcoat blistering.

C-3

water to the fibre–resin interface and the leaching of water-soluble substances from the fibre surfaces. The possibility of leaching of cations from E-glass fibres is well established, and leaching of sodium from carbon fibres has been proposed.

The nature of the solutes giving rise to osmosis depends on the precise circumstances. It will be a major feature of this discussion that several specific solutes will be identified, with specific confirmatory evidence of their presence in the composite samples, and others will be postulated. These details will be found under the appropriate sections below.

3.3. DISC CRACKING IN RESINS

1967

3.3.1. Occurrence

Steel[10] observed that unstressed castings of polyester resins showed gross disc cracking when exposed to hot water for long periods of time. He studied the kinetics of crack formation and suggested that plots of crack initiation time against temperature followed the Arrhenius relationship, being linear down to 40°C for at least one resin, with an activation energy of about 100 kJ mol^{-1}. These plots are reproduced in Fig. 3.3. Steel observed that for a given resin, cracking always occurred at the same water absorption level, and deduced that (at least in some cases) cracking would never occur at ambient temperatures, since the critical water uptake level would exceed the equilibrium absorption value. Another conclusion emerging from this study was that the crack initiation time increased slightly with post-cure time.

??

The explanation offered by Steel concentrated on the rupture of polyester chains either by swelling forces or by the hydrolytic scission of ester groups. The hydrolysis would require a roughly comparable activation energy (46–84 kJ mol^{-1}) and would occur at those chain segments most strained by swelling. No mention was made of osmosis or of the reason for the distribution of cracks within castings. Postcure was thought to increase crack initiation time by promoting crosslinking. An alternative explanation seems more probable if the osmotic explanation is accepted. Postcure drastically reduces the quantity of free styrene in the resin. Although styrene itself has a low solubility in water, and would not provide much contribution to the total osmotic pressure, its oxidation to benzaldehyde could produce significant quantities of solute.

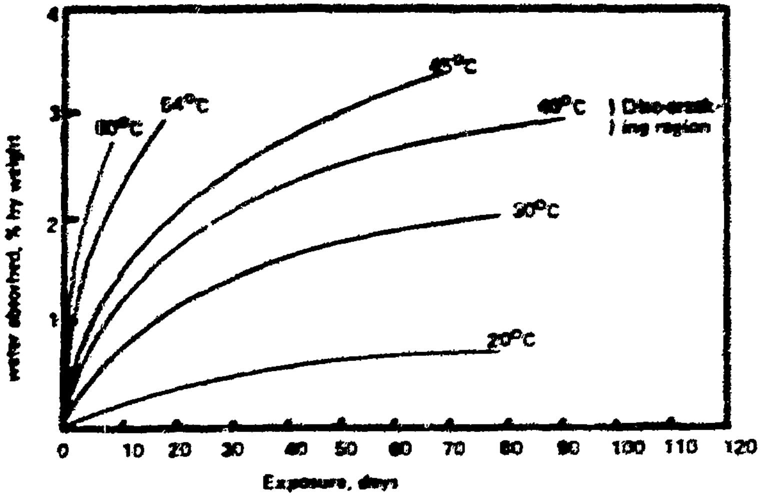

FIG. 3.3. Rate of disc crack initiation in polyester castings as a function of water temperature. (After ref. 10, courtesy of the Plastics and Rubber Institute.)

3.3.2. Inorganic Inclusions

9 67

About the same time as Steel was reporting these findings, another study by Ashbee *et al.*[11] was directed to the same disc cracking phenomenon. The cracks, in unsaturated polyester resins, were studied by optical and electron microscopy. The size, number and orientation of these cracks were different in different polyester resins. Sometimes the orientation was random, but in other cases most of the cracks were roughly parallel to the specimen surfaces. These authors proposed that the cause was osmosis arising from water-soluble inclusions, and attempted to identify the inclusions by electron probe x-ray microanalysis. This technique allows for the examination of micron-sized areas of specimens and records the presence of elements from atomic number 12 (carbon) or, with some instruments, 9 (fluorine) to 92 (uranium) or thereabouts. Examination of the origin of some of the internal cracks by optical microscopy showed that there was some undissolved impurity present, and the electron probe microanalysis indicated the presence of small quantities of potassium, chlorine, sulphur and calcium.

The uncured resins were then dissolved in chloroform and the

water-soluble substances extracted for subsequent analysis by flame photometry. After correction for blanks, it was found that the sodium concentrations ranged up to 20 ppm at most, while calcium and potassium concentrations were generally less than 10 ppm.

$\Pi V = nRT$

An attempt was made to estimate the magnitude of the osmotic pressure produced by various concentrations of potassium chloride, using eqn (1) above. Accordingly, it was deduced that sufficient pressure could be generated to crack the resins.

(It should perhaps be pointed out that although the overall concentration of a solute in a mass of resin may be very low, nevertheless the concentration in the vicinity of an inclusion can still be very high.)

However, many resins contain traces of chlorine, sodium, potassium and other elements without forming disc cracks. The likelihood is that the impurities responsible for most of the osmotic sites in organic polymers will be organic substances of high water solubility. The technique of electron probe microanalysis does not detect or identify such substances.

Ashbee *et al.* demonstrated that doping resins with 100 ppm water-soluble inorganic salts accelerated the rate of cracking during immersion in boiling water, and when a very deliquescent salt (calcium chloride) was used, cracks eventually appeared even in samples which had not been immersed in water. On the other hand, cracking was suppressed by boiling in a saturated salt solution, as would be expected if the mechanism is osmotic.

Salt water
boats, ship
blister

3.3.3. Disc Cracks in Laminates

Pritchard *et al.*[12] reported the time taken to produce disc cracks in polyester glass laminates exposed to hot water on one side only, as in a tank or pipe. Most of the cracks were confined to the region just below the surface exposed to water. The surface regions also underwent a different kind of cracking, probably as a result of shrinkage through further cure.

3.3.4. Organic Residuals

1982
Edwards
et al

An extensive study of disc cracks in orthophthalic and isophthalic polyester castings and in a vinyl resin was carried out by Abeysinghe *et al.*[13] They observed the time of initiation of the cracks and noticed that it depended very much on the concentration of the free unreacted glycol in the polyesters. For example, addition of about 5% w/w glycol in the polyesters. For example, addition of about 5% w/w propylene glycol to an uncured isophthalic polyester reduced the

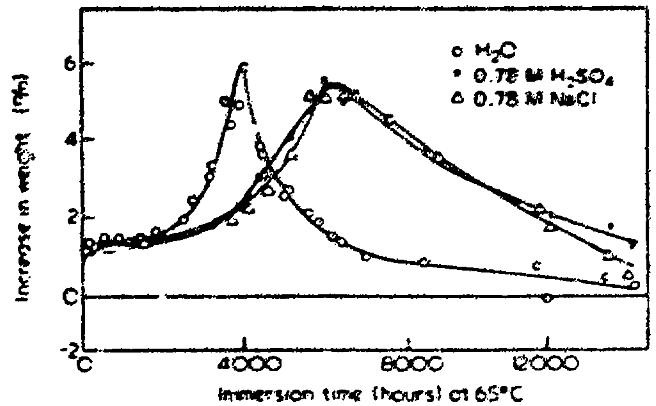

FIG. 3.4. Overall weight increase of crosslinked unsaturated polyester resins immersed in various aqueous solutions. (Reproduced from ref. 13, by permission of Butterworth and Co. Ltd.)

initiation time from 2000 h at 65°C to little more than 100 h. Conversely, removal of all the traces of residual glycol present at manufacture increased the initiation time substantially. Addition of water-insoluble hydrocarbons had no effect.

Immersion in dilute salt solutions confirmed the previously reported observation that initiation time increased with solution concentration. Plotting the observed weight increase against time gave sharp peaks, as shown in Fig. 3.4. These peaks were preceded by a more gradual increase in weight, at a time corresponding to the crack initiation time. It seems probable that a rapid inflow of water occurred through the cracks, leading to increased exposure of fresh resin surfaces, accelerated hydrolysis, leaching and weight loss. Substantial quantities of a white, crystalline substance could be seen around the crack edges; its infrared spectrum resembled that of isophthalic acid.

Subsequent drying out of the powdered resin indicated net weight losses through leaching. After correction for leaching losses, the water absorption curves became more sigmoidal, with the usual plateaux. Nuclear magnetic resonance (NMR) spectra of deuterium oxide extracts from several polyester resins showed that the quantity of fumaric acid in the leached substances was low, but there was plenty of isophthalic or orthophthalic acid and free glycol. The latter was confirmed by gas–liquid chromatography.

It therefore seems probable that organic residuals play a large part

in the generation of disc cracks in polyesters. The presence of free glycol at the 1% level is well known. Such large concentrations would probably swamp any effects related to the presence of inorganic salts in resins as previously discussed. Significantly, the above-mentioned workers found no cracking in the vinyl ester resin, which is made without glycol.

Glycols are not the only organic substances found to promote disc cracking in polyesters. Abeysinghe *et al.*[14] recorded the initiation time for several other water-soluble substances, deliberately added, and found that dimethyl formamide and dimethyl sulphoxide were even more effective. Acetone, surprisingly, was not such an effective crack promoter, possibly because of its volatility.

3.3.5. Epoxy Resins

The formation of disc cracks in epoxy resins is relatively uncommon. Three explanations for this observation can be considered. Firstly, there are fewer water-soluble residual substances present; secondly, the permeability to water is very much lower, so crack initiation would in any case take a great deal longer; and finally, the stress required to initiate cracks in epoxy resins is higher than in conventional polyesters. These explanations will now be considered.

There is no glycol in glycidyl ether type epoxy resins, and any other potential residuals are either of low water solubility, or potentially capable of becoming chemically bound into the network during cure, so that what remains is present at only a very low concentration. One possible source of an osmotic solute is the curing agent, however. Usually, nearly all of the curing agent reacts, but if there is a mixing problem, or the curing agent is not readily soluble in the uncured resin, then there may be small quantities of unreacted material left over. Small particles of solid curing agent are likely to become 'sealed' at an early stage by the formation of a skin of crosslinked resin, which makes any chance of reaction for the rest of the particle within the skin somewhat remote. Some common curing agents, such as dicyandiamide[15] and some anhydrides,[16] are soluble in hot water and therefore fulfil the criteria for giving rise to osmotic pressure pockets. Interestingly, dicyandiamide not only dissolves in hot water, it also reacts with it, producing ammonia.

The first argument, therefore, leads to the conclusion that osmotic effects will normally be absent from epoxides, but not in every case; the outcome would depend on the curing agent and, in the case of solvent-based systems, on the presence of residual solvent. The second argument is more general. The rate at which water diffuses into epoxy resins is much lower than that for polyesters. On the other hand, the total quantity of water absorbed by epoxy castings after prolonged periods is surprisingly high—often 4–7% w/w[17,18]—so it seems that the low permeability simply delays any effects associated with water uptake. Polyester values are often lower but the published values are sometimes less than the true water uptake values because they are offset by considerable leaching.[19] Epoxies do not contain hydrolysable ester groups and so the water has less scope for producing fresh osmotic solutes by hydrolysis. The accommodation of water in crosslinked epoxides is a complex matter; it appears probable that much of the water is bound to hydroxyl and other polar groups, rather than in the free state.[20–22]

The fracture toughness of epoxy resins is variable, depending on resin structure, and on the measurement technique. Some typical values have been given, along with those for polyesters, by Pritchard and Rhoades.[23] The toughness of epoxides is not vastly higher than that of polyesters when expressed in terms of the critical stress intensity factor, but other criteria suggest a somewhat larger differential. On the whole, the ease of crack initiation seems an unlikely reason for the ready disc cracking of polyesters compared with epoxies.

Disc cracks have been deliberately induced in an epoxy resin, MY 750 (Ciba Geigy), cured with TETA (triethylene tetramine). This was done by adding a water-soluble ketone solvent such as diethyl ketone. The initiation time was very much longer than usually observed with polyesters and when the cracks finally appeared, they looked different.

3.3.6. Critical Pressure

1982 ✓

Walter and Ashbee[24] calculated the critical osmotic pressure necessary to initiate disc cracks. They considered the energy change associated with the inflation of a penny-shaped crack to be the sum of an elastic component,

$$-E_{\text{elastic}} = -(2\pi p_i^2 ab^2)/3E \qquad (3)$$

where a = crack half thickness, b = crack radius, E = Young's modulus of the resin and p_i = pressure, and a surface component

$$E_{\text{surface}} = 2\gamma\pi ab \qquad (4)$$

where γ = specific surface energy.

So the total energy

$$E_{\text{total}} = (2\gamma\pi ab - 2\pi p_i^2 ab^2)/2E \qquad (5)$$

and, considering the differentials with respect to a and b, it was deduced that the critical condition was

$$p_i = ((3E\gamma)/b)^{1/2} \qquad (6)$$

which gives a rather high value for p, unless E and γ are assumed to be lower than the usually quoted values. In fact the operative values could well be lower. Young's modulus values for dry polyester resins are generally of the order of 3 GN m^{-2}, measured in ordinary testing machines at crosshead speeds of about 2 mm min^{-1}. Soaking in water at 65°C for over a year reduces the modulus to about half its dry value. The modulus at the temperature of immersion could be about the same as its ambient temperature value, or alternatively it could be substantially lower, depending on the temperature of the glass transition. However, immersion in hot water alone, even for long periods, would not reduce the modulus by a very substantial amount. A more promising idea is that the resin, being viscoelastic, shows a much lower modulus at very low strain rates than it does under normal test conditions. The formation of a disc crack corresponds with very slow rates of strain. It therefore seems probable that the appropriate value of E is much less than 3 GN m^{-2} and the critical pressure required to produce a crack of radius 10 μm would be only a few MN m^{-2} at most. Such pressures can be generated by dilute solutions of organic or inorganic substances such as those expected in this context.

3.3.7. Crack Size, Orientation and Distribution

1980

The tendency of some resins to form randomly orientated cracks and others to show a preferred orientation, has already been mentioned. Abeysinghe[25] examined the cracks in one isophthalic resin under a variety of immersion conditions. Specimens approximately 80 × 20 × 3·5 mm showed randomly orientated cracks, about 300 μm in diameter, near the surfaces, but the central core contained larger cracks of about 700 μm diameter, and these were mainly oriented parallel to the plane of the major surfaces, probably as a result of the swelling stresses induced during immersion. Immersion in dilute sodium chloride and in dilute sulphuric acid solutions altered the fraction of the total volume associated with each crack type, increasing the quantity of the larger and oriented cracks. Sometimes the edges of the specimens were relatively free of cracks, suggesting that the water-soluble organics had leached out before high pressures could be generated. Very small (40 μm) cracks appeared slowly after immersion in relatively concentrated solutions. These cracks were mainly near the surfaces.

The size of the cracks increased with time, but eventually stablised. Upon drying, some of the smaller cracks, and those in samples which had not undergone exceptionally prolonged immersion, tended to become smaller, but cracks in specimens subjected to long immersion periods remained.

FIG. 3.5. Fracture surface of a centre-notched polyester specimen containing disc cracks, showing randomly oriented ridges.

3.3.8. Fractography

Fracture surfaces of disc-cracked resins showed randomly oriented ridges (Fig. 3.5). The fracture toughness was raised slightly when disc cracks first appeared, but it fell again after more prolonged immersion as the cracks became so numerous that the stress fields around them interacted.

3.4. GELCOAT BLISTERING IN LAMINATES

3.4.1. Occurrence

Glass–polyester laminates used for the construction of boat hulls sometimes develop small blisters in localised regions below the waterline. The kind of blisters discussed here are those which develop slowly as a result of immersion in water, and should not be confused with those occasionally observed in new hulls as a result of fabrication faults. It is commonly found that small, lightweight craft, such as canoes, are free from blisters, because they are lifted from the water after use, whereas boats of 10 m in length remain in the water for months at a time. The extent of the problem is almost as much a matter for controversy as the cause; some reports indicate that only a few percent of all polyester boats suffer from noticeable blisters,[26] while others suggest that the defect is more common.[27] Blisters have also been observed in swimming pool liners and in chemical process equipment.

Figure 3.2 shows a proposed mechanism for the formation of osmotic blisters. The diagram illustrates a lay-up of chopped strand mat reinforcement, with a gelcoat and a multicoat paint treatment. Water penetrates through the paint layers and the gelcoat, until it reaches the interface between the gelcoat and the backup laminate. In theory, the quantity of water arriving at this interface should be uniform, but in practice, certain regions of the interface receive more water, because of the presence of non-uniformly distributed solutes which collect in microcavities within the gelcoat and within the boundary region between gelcoat and laminate. These regions become the sites of blistering. The same kind of effect could produce blisters between

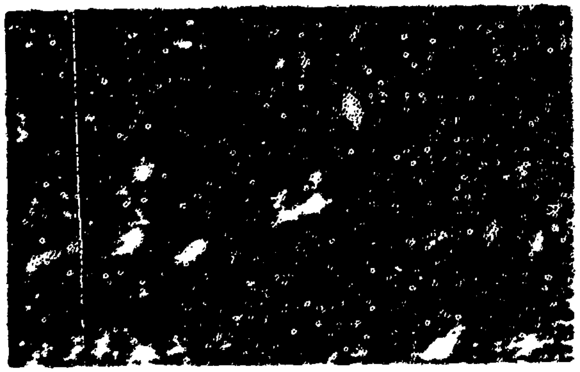

FIG. 3.6. An example of a gelcoat blistering in an orthophthalic/chopped strand mat laminate with an isophthalic gelcoat.

successive paint layers. An example of gelcoat blistering is shown in Fig. 3.6.

Many laboratory and field trials have been performed, and have given general indications of how to avoid, or at least minimise, blistering in marine laminates. More recently, analytical evidence has been presented, showing the nature of the solutes present, and indirectly, the cause of the problem. It is therefore possible to see why the various coupon tests reported over a number of years gave the kind of results observed. These experiments will now be reviewed briefly, starting with an account of a number of studies of factors affecting blistering rates.

3.4.2. Factors Affecting Blistering Rates

3.4.2.1. Gelcoats

The rate at which water penetrates the gelcoat is important, and early investigations of the blistering process emphasised the gelcoat composition.[28] Isophthalic resins are superior to those made from phthalic anhydride in this respect,[29] and have now become much more widely used. Economics prevents their more widespread use in the backup laminate, but the first layer of glass reinforcement may be impregnated with an isophthalic resin. Other structural features of importance in gelcoat resin synthesis include the nature of the glycol. 2,2,4-Trimethyl-1,3-pentanediol has been advocated for improved water

resistance,[30] and 2,2-dimethyl-1,3-propanediol (neopentyl glycol, NPG) has been specifically claimed to reduce blistering.[31] The molecular weight and molecular weight distribution of polyesters affect their water resistance too.[32]

Some investigators have concentrated on the quality of the gelcoat, rather than its chemical constitution. Strocks[33] noted the tendency of the gelcoats to result in early blister development, and mentioned the probability of a link between blisters and tiny air bubbles within the gelcoat layer. Lüttmann[34] discussed the relationship between gelcoat quality and fabrication conditions; for example, a working temperature below 18°C results in much increased viscosity, trapped air-bubbles, and uneven thickness. Gelation is delayed too, so the evaporation of styrene is excessive and insufficient of it remains for proper cure.

Using a brush to apply the gelcoat inevitably leads to uneven thickness as well, and the combination of insufficient styrene with surface inhibition means that some parts of the gelcoat never crosslink adequately. Spraying gives a more uniform thickness, but many more air bubbles are also introduced, and these will escape only if the viscosity is low enough.

The time interval between applying the gelcoat and the laminate is important, and delays of more than an hour or two are undesirable. Lüttmann also mentions the adverse effect on the gelcoat hardening process of any residual solvent (alcohol or water) left over from a polyvinyl alcohol release agent solution, especially when the laminate is made in rather cool, humid weather. The result is again an undercured gelcoat.

1980

Norwood *et al.*[35] report that an isophthalic gelcoat resin of medium heat distortion temperature performed better in water at 40°C than one of rather lower heat distortion temperature. Also the isophthalic resin made from NPG was better than ordinary isophthalic resins because of the steric hindrance to hydrolysis provided by this kind of structure.

3.4.2.2. Pigment

The same researchers recommended that the isophthalic/NPG gelcoat should be white or clear, and that deeply coloured gelcoats should not be used below the waterline. This was because white pigment pastes were generally dispersed in gelcoat resins, whereas dark pigments were frequently supplied in low molecular weight, hydrolysable diluent vehicles. This advice supported that of Tyler[36] who recommends gelcoats free from any particulate additive, whether pigment or fire retardant.

In addition to their carrier liquid, some pigments have the disadvantage of increasing the number of interfacial capillary channels by which water can penetrate the resin. The water resistance of pigmented paint films has been studied by Krause[27] and some of his conclusions are relevant to the glass-fibre reinforced plastic (GRP) case.

3.4.2.3. *Lay-up Resin*

The same principles apply for lay-up resins as for gelcoats, but they are not directly in contact with water, and since they form the bulk of the laminate, it is not possible to use the more expensive materials. As

1977 Edwards[28] points out, however, the gelcoat is permeable, and the lay-up resin therefore has to be able to withstand water. Edwards suggests that the permeability of the laminate should be made greater than that of the gelcoat, to avoid a buildup of water at the interface between the two. The laminates he tested always showed a tendency to blister if they contained orthophthalic resin, even with NPG as glycol.

77 Strocks[32] recommended that lay-up resins of low acid value and low hydroxyl value (i.e. high molecular weight) should be used immediately behind the gelcoat, to a thickness of 1 or 2 mm. High molecular weights are achieved more easily in practice with isophthalic formulations.

3.4.2.4. *Glass Reinforcement*

Most of the discussions about the role of the glass reinforcement in blistering have assumed that the reinforcement is in the form of chopped strand mat. Unless otherwise stated, this chapter does the same. Reinforcement glass fibres are usually E-glass, though occasionally S-glass is employed in high performance composites and C-glass is used as veneers for chemically resistant laminates. The effects of using glass fibres of different compositions have not been reported in the literature, but it is well known that S-glass is more resistant to water. A more important variable in practice is the kind of treatment to which the filaments are subjected.

Different samples of glass fibre vary in bundle tex (number of filaments per strand), in coupling agent and in size (which for convenience will be taken to embrace all the coating material on the fibres, except the coupling agent). The substance used to bond the chopped fibres into mat form is known as the binder, and constitutes a larger part of the total weight of additives than the other substances.

Most of the attention of investigators has concentrated on binders. Two main categories of binder are widely used: emulsions based on polyvinyl acetate (PVA) and powders derived from Bisphenol polyester resins. The most important difference between these two is their ease of hydrolysis; the PVA emulsion is slowly hydrolysed to form acetic acid, which can be detected in the aqueous fluids within blisters. The difference in the blistering rate is more marked above 40°C than at ambient temperatures.[20]

It has sometimes been noticed that improved performance is obtained with low bundle tex and a low surface density. This gives increased ease of impregnation and lower microporosity.

The influence of the coupling agent has not received much attention in this particular context, although its importance in promoting the water resistance of the composite as a whole is beyond dispute.

Norwood *et al.*[25] reported that powder bound mats were superior to emulsion types, except with NPG gelcoats, but pointed out that the powder-bound variety can be much more difficult to use in hand lay-up. They found that a surface tissue improved the behaviour of the laminates by improving the effectiveness of the resin rich barrier. They also used laminate constructions containing some woven roving. Van

1980 der Beek *et al.*[29] also investigated the role of the glass reinforcement and found powder bound mats preferable to emulsion ones.

3.4.2.5. *Catalyst Systems*

The most frequently used catalyst (or initiator) system for polyester resins is probably the hydroperoxide-cobalt(II) redox system (see Fig. 3.7(A)). Alternative initiators include benzoyl and other peroxides, alone or with a tertiary amine (see Fig. 3.7(B)), and the peroxyketals[40] (see Fig. 3.7(C)). The influence of the initiator on the blistering behaviour of laminates may be seen in differences between these various systems, and there have been reports of the effect of concentration of initiator on blistering rate. Two explanations for the findings generally observed may be considered. One is that some initiator systems give a better approximation to complete cure, and therefore a less permeable and less easily hydrolysable resin. The other is that initiators do not completely disappear, but become converted into other substances, some of which are capable of acting as osmotic solutes. There is a third consideration: most promoters and initiators are dispersed in diluents

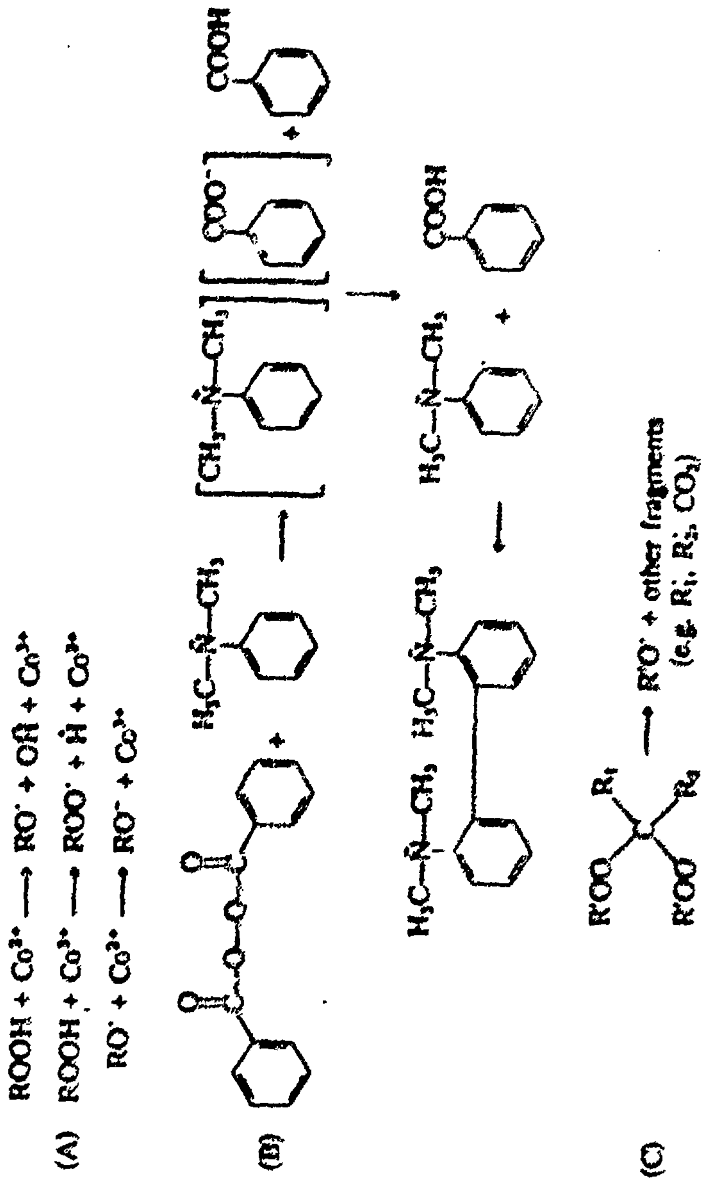

FIG. 3.7. Mechanisms for polyester initiating systems, showing their potential for generating water-soluble products.

of some kind, and the quantity may be more than 1% of the weight of the entire laminate. Usually, the substances are phthalates, which are not very soluble in cold or moderately warm water and therefore have little or no role in blistering.

1979

Edwards found that the rate of blistering was decidedly dependent on the amount and type of free radical catalyst. Blistering was lessened as the quantity of the peroxide was reduced (the promoter concentration was increased to keep the gel time constant throughout). Cast resins made with various catalyst concentrations also showed inferior resistance to boiling water as the catalyst level increased.

Euchner *et al.*[28] also found that blistering and water resistance deteriorated when the quantities of cobalt accelerator and methyl ethyl ketone peroxide (MEKP) were seperately increased. Lüttmann[34] suggests that, although MEKP/cobalt(II) represents the most widely used catalyst system, it does have disadvantages, since the quantities required to give satisfactory cure can lead to short gel times and inadequate impregnation in hot weather, with consequent microporosity or inadequate wet-out. Cyclohexanone peroxide offers advantages in this respect.

Platell found that glass–polyester swimming pools containing blisters also suffered from brown to black stains in the vicinity of the blisters.[41] The stains were apparently caused by reaction between the cobalt ions in the blister fluids and the chlorinated pool water, which penetrated any cracked blisters and oxidised the cobalt.

Strocks found no significant difference beteen the blistering behaviour of laminates hardened with MEKP, acetyl acetone peroxide and benzoyl peroxide.[33] The levels of peroxide or hydroperoxide used were, however, quite important and laminates with too much or too little hardener were decidedly more prone to blister development.

1983

Davis et al.[42] found less favourable results with the benzoyl peroxide/tertiary amine system than with the cobalt/MEKP one. No single cause was established, but the possibilities previously mentioned, i.e. differences in cure state, and the production of hydrophilic end products, were considered.

3.4.2.6. *Fabrication Procedures*

It will already have become apparent that the kind of fabrication methods adopted are important in the production of high quality laminates, and it is not just a question of using the right materials. Control of gelcoat thickness, degree of cure and adhesion to substrate

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a GRP pool, and detected mostly calcium, with a little cobalt in the ash from an ignition test. Swabbings from stained areas of the gelcoat also contained mostly calcium, but with iron, manganese, cobalt and copper at lower concentrations.[41]

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3.5. Cations

Abeysinghe *et al.*[14] summarised the analytical results from a major survey of the contents of the fluids in blisters from several hundred panels. The metal cations were analysed using samples of fluid extracted by means of hypodermic syringes, directly from the blisters. The analytical techniques employed were atomic absorption spectroscopy (AAS), flame photometry (FP), and for qualitative data only, energy dispersive analysis by x-rays (EDAX). Table 3.2 shows some typical results. The determinations by AAS and FP were always in broad agreement.

Large calcium concentrations were found, sometimes of more than 4000 ppm. Other cations of the kind related to E-glass were present in much lower concentrations. There were also small quantities of some cations not normally expected in E-glass at a significant level. Cobalt (presumably from the promoter), iron (believed to be from the water immersion heater or pump) and zinc were detected.

TABLE 3.2
TYPICAL CONCENTRATIONS OF METAL CATIONS IN BLISTER FLUIDS FROM GRP
(from ref. 14)

Cation	*Technique*	*Time (days)* (45°C)	*Typical concentration (ppm)*
Sodium	FP	120–240	50–250
Potassium	FP	120	200–250
Potassium	FP	220–270	150–225
Calcium	FP	120	2500–4650
Calcium	FP	240–270	1350–6350
Calcium	AAS	120	2650–3500
Calcium	AAS	240–270	1500–7600
Magnesium	AAS	120	200–560
Magnesium	AAS	240	100–640
Zinc	AAS	240–270	50–100
Aluminium	AAS	120	430–625
Aluminium	AAS	240–270	425–790
Iron	AAS	120	85–100
Iron	AAS	240–270	50–130
Cobalt	AAS	120	110–120
Cobalt	AAS	240	110–175
Copper[a]	AAS	120	20
Copper[a]	AAS	240	8

[a] Only a few estimations were made of copper.

Supposing that the majority, but not all, of the cations found originated in the E-glass fibres, it seems likely that there would be a short induction period before their appearance, while water penetrated the glass fibre coating. Thereafter, the longer the exposure time, the more the concentration might be expected to increase. On the other hand, the inflow of water into a blister obviously dilutes any solutes present. It would be of interest to monitor the concentration of a single species, such as calcium, throughout the blistering process for a given laminate, under standard conditions. The immersion time is important and it should be noted that the data in Table 3.2 cover a wide range of times.

Hsu *et al.*[46] studied the rate of dissolution of magnesium, aluminium and silicon from S-glass powders in water at 40°C and found that dilute ammonia solutions enhanced the dissolution of magnesium, and particularly of aluminium. Ammonia is to be expected in small quantities in laminates containing certain nitrogen-based substances. Nevertheless the pH of blister fluids is generally less than seven—typically 3–5. Acidic media, too, can attack glass surfaces, although the mechanism is different, and initially involves hydrogen ions replacing alkali metal ions in the surface.[47,48]

3.5.5. Organic Constituents

Abeysinghe *et al.*[14] also analysed the organic constituents of the blister fluids, using gas liquid chromatography (GLC). This required an extensive programme of peak identification by seeding with suspected substances, taking account of the probable fate of the various constituents of the laminates. A thorough knowledge of all the materials used in the resin formulation and in the laminating procedure, together with all the information about the history of the laminates and their exposure conditions, was essential in view of the large number of possible substances involved.

Figure 3.8 shows a chromatogram obtained from a blister fluid, and the numbered peaks are identified in the discussion below. Other peaks remain unidentified. No attempt was made to analyse for trace residual acids. This was because (a) it would require more difficult and time-consuming derivatisation procedures,[49] which could have proved

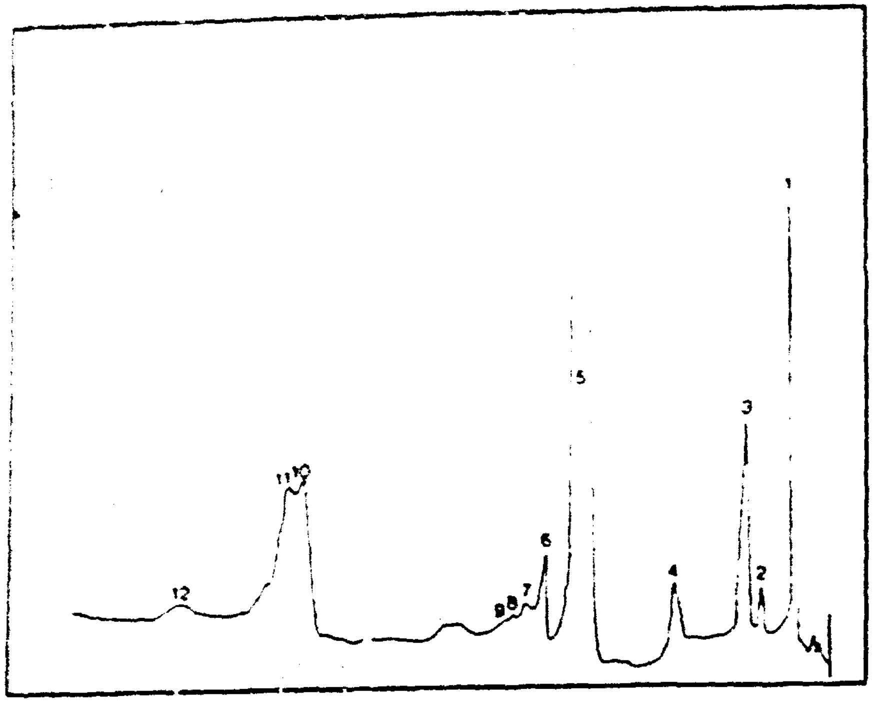


FIG 3.8. Gas-liquid chromatogram of the blister fluids from an emulsion-bound laminate. Peak numbers are explained in the text.

impractical in the circumstances, (b) fumaric acid was thought to be present only in small concentrations and (c) phthalic acid was thought not to be sufficiently soluble in cold or moderately warm water to make much contribution to osmosis.

The origins of the GLC peaks in Fig. 3.8 will now be considered.

Methyl ethyl ketone (peak 1) is probably formed by decomposition of the MEKP promoter, which is itself a complex mixture of hydroperoxides,[50] formed by reaction between methyl ethyl ketone and hydrogen peroxide. The size of this peak was larger than expected. This observation would explain those made by other workers, already mentioned above, that excessive catalyst levels are deleterious. The MEKP diluent, a phthalate, was not looked for, and not thought to be important. Adding large quantities of extra dimethyl phthalate did not increase the rate of blistering.

Benzene (peak 2), toluene (peak 4), ethyl benzene (peak 6) and the three isomeric xylenes (peaks 7,8 and 9) were all found but the peaks

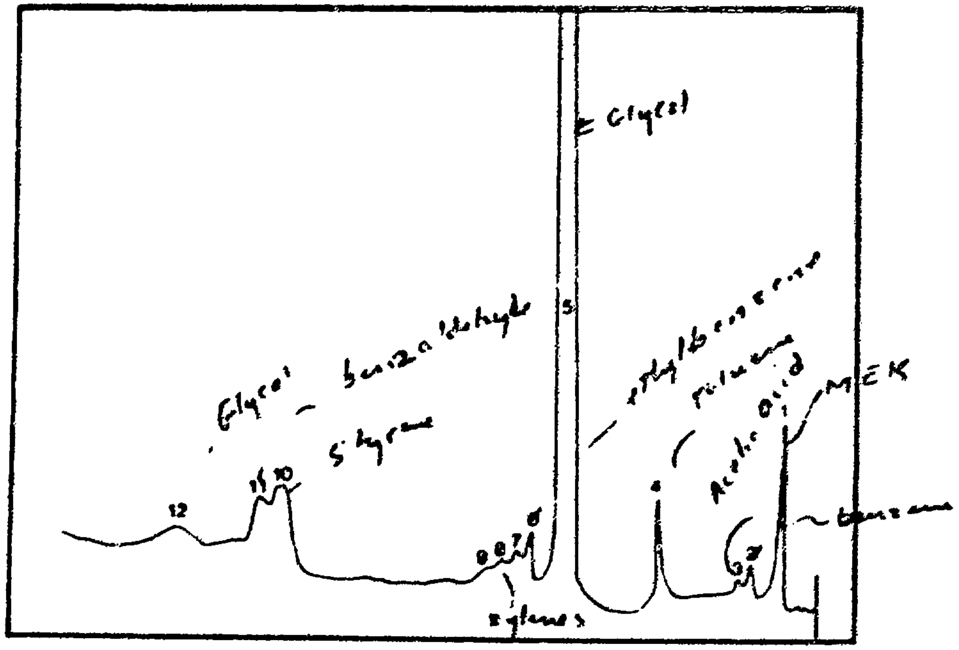
were small and, although the analysis was not quantitative, it can be assumed that the quantities of these substances were also small. They were probably impurities in the styrene monomer,[51] which is known to contain small quantities of all these substances,[4] along with others. Other styrene impurities not identified in this chromatogram are α-methyl-styrene, which polymerises rather slowly under free radical conditions, and cumene. The xylene isomers could also have originated from the azeotrope used in making the resin.

Peak 10 corresponds with styrene itself. None of the hydrocarbons mentioned is very soluble in water, and none is thought to be very important in connection with osmosis. Styrene for example has a solubility in water of about 250 ppm at ambient temperatures.

However, styrene oxidises readily to form aldehydes[52] which are more soluble in water and so capable of generating osmotic pressure. They can also oxidise to acids. It has already been noted that benzaldehyde could often be recognised by its smell; the mechanism for its formation is well known. Peak 11 corresponds with benzaldehyde in Fig. 3.8.

Peak 3 refers to acetic acid, which is widely believed to result from the hydrolysis of polyvinyl acetate emulsion binder. Some powder bound mats are also treated with dressings containing very minute traces of acetate, or have sizes in which the pH is adjusted by means of acetic acid. Nevertheless, the main source of acetic acid is almost certainly the binder and the quantity of acetic acid from powder bound mats can probably be neglected. The GLC chromatogram from a laminate similar to that associated with Fig. 3.8, but made from a powder bound mat instead of an emulsion one, is shown in Fig. 3.9. There is hardly any detectable peak in Fig. 3.9 at the position corresponding to peak 3 in Fig. 3.8.

The remaining identified peaks, 5 and 12, both refer to free glycol. The orthophthalic laminating resin was made from propylene glycol (peak 5) and the isophthalic gelcoat was made using both propylene glycol and diethylene glycol (peak 12). Normally, a little glycol remains unreacted, and can be removed by vacuum stripping, or left as a minor constituent of the resin. Sometimes it is considered advantageous to leave a small quantity, or even to add extra, in order to adjust the viscosity. In this case, GLC extraction tests showed that both the lay-up and the gelcoat resins contained small quantities of unused glycol. Trials were carried out to determine the effect on the blistering rate of adding more. It was found that this was more important, on



1983

FIG. 3.9. Chromatogram of the fluids from a blister in a powder-bound mat laminate.

1981

balance, than any other single factor.[33] Figures 3.8 and 3.9 have large glycol peaks, simply because in these cases some extra glycol was added. In these particular laminates, 2·5% extra propylene glycol was added to the laminating resin and 2·5% extra diethylene glycol to the gelcoat resin.

The possibility of interaction between the various substances while still in the blister, or later during storage in glass ampoules, or again while on the GLC column, is considerable and makes any attempt at drawing quantitative conclusions very dubious. One example is the possible reaction between glycols and acetic acid.

3.5.6. Effects of Painting

Most GRP boats, and some other GRP structures, are painted, for cosmetic or antifouling reasons. The transport of water through paint films has been investigated by Perera and Heertjes,[9,54] who found that

blistering of the paint layer itself could occur more readily in distilled water than in sea water. This is consistent with an osmotic explanation.

When GRP is painted, the surface is first abraded to remove residual release agents, etc., and a primer is then applied, followed by a number of coats of undercoat and topcoat. The damage done to gelcoats by chemical paint removers prior to repainting, and even by the etch primer, was said by Tyler to be a major cause of osmosis;[36] the dangers of etch primers were also mentioned by Norwood *et al.*[35] The rationale is that etch primers contain chlorinated solvents which, if allowed to remain in contact with the gelcoat, could soften it and make it more permeable.

Ghotra and Pritchard[55] investigated the effects of several painting systems on the rate of blistering of the same laminates previously mentioned in the analytical study of blister fluid contents.[14] The use of an etch primer alone did not have any significant effect on blistering rates. Generally, paint schemes without conventional primers formed blisters between the paint and the gelcoat. Many of the other paint schemes used also suffered from inter-coat blisters after prolonged immersion at 45°C, and very few painting systems delayed the blistering process much when the inter-coat blisters were taken into account as well as proper gelcoat blisters. Cation concentrations in the blister fluids were rather less than in the unpainted laminate blisters. The worst results were obtained when an antifouling paint was overpainted with an acrylic coat which, in the absence of the antifouling, had caused no problem. Interaction between paint constituents would be very difficult to predict.

3.6. REPAIR OF BLISTERS

The renovation of blistered GRP structures can be expensive, and is justified only if the extent of the defect is substantial. A statement on the remedial work necessary has been issued by the British Plastics Federation,[56] together with a classification. The smallest kind of blisters, up to pinhead size, have little significance unless and until they are seen to be growing, which does not always happen. The kind of blisters, previously mentioned, which follow the line of the glass fibre bundles require end of season attention, using stopping compounds, and subsequent painting. Their development is progressive from a train of tiny blisters to a long ridge, cracked at the apex.

Larger blisters, 5–15 mm in diameter, may still not be important if no glass fibre pattern is visible beneath their broken surfaces. However, any blisters already broken require repair, by sanding down, washing, drying out, stopping and painting.

The presence of glass fibres visible under broken blisters is considered important only in the case of blisters which have reached 5 mm diameter, provided that the fibres are well coated with resin. The larger blisters require scraping out, cleaning, washing, thorough drying, stopping and painting.

The more serious kinds of blister are those which, when cut open, expose fluffy or resin free fibres, and therefore necessitate the cutting back of the affected part and its replacement by additional layers of glass mat with fresh resin, or in localised regions, by a dough of resin mixed with glass fibres.

Large (10–50 mm) blisters are sometimes found, associated with a deep void within the laminate where water has accumulated and distended the surface, raising it to form a broad, flat blister. Again, this requires the removal of any dry glass fibre to reach the level where well impregnated reinforcement can be found, before building up with new resin and glass mat.

These operations are time-consuming and require some experience if the hull is not to be damaged by the use of inappropriate techniques for removing the affected region. Failure to dry the affected area completely can result in water evaporating during the heating caused by the cure of the filling resin, and thus a new region of porosity is introduced.[57]

3.7. OSMOTIC DEBONDING

1971 Ashbee[58] proposed that debonding of glass fibres from a resin matrix could be associated with the generation of osmotic pressure around water soluble constituents leached from the fibres. Cracks were observed growing into the resin from the interface and also on surfaces parallel to the fibre axis. These cracks were especially extensive in C-glass fibres, which contain substantial quantities of sodium. The sodium in glass fibres is easily removed by aqueous liquids, and produces an alkaline medium capable of further attack. Later, Vaudin and Ashbee[59] measured the ability of the glass–resin interface to withstand water immersion, as a function of glass composition, and the

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nature of the chemical environment in which the fibres were drawn. Interfacial osmotic pressure pockets were eventually formed after various intervals. These pockets formed particularly rapidly in the case of S-glass drawn into an atmosphere of ammonia. The explanation proposed was that ammonium and bicarbonate had formed as a result of reaction between ammonia and carbon dioxide trapped within the glass during its manufacture.

If this kind of mechanism is accepted as a major contributor to fibre–resin debonding, it follows that the ideal fibre should be completely inert to water. Carbon fibres might be thought sufficiently inert, although sodium has been reported in some polyacrylonitrile-based carbon fibres too,[60] arising either from polymerisation additives or from the spinning solvent.[61] The quantities present are small, and the problem appears less serious than that observed with glass.

Essentially similar processes can be expected when resins containing particulate fillers, having soluble trace impurities, are immersed in water. The breakdown of resin–filler interfacial bonding would be expected.

3.8. CONCLUSIONS

Osmotic pressure pockets occur widely in organic matrix composites exposed to water. The pressure generated is sufficient to make a significant contribution to the eventual deterioration of these materials after long periods of severe environments. The best remedy is a gradual replacement of all the water-sensitive constituents of laminates—especially in and immediately behind the surface contacting the water—by materials impermeable to, or inert to, water throughout the range of operating temperatures envisaged.

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ALAN C. OLFORD

OSMOSIS

CAUSE AND EFFECT

As you will no doubt be aware, there has been growing concern in the past months over the apparently increasing number of G.R.P. vessels found to have blistering of the underwater gel coat surface.

The general term now common for this condition is "Osmosis" although in precise terms not all blistering is as a direct result of this phenomena.

Various articles appeared in the popular yachting press throughout 1976 and 1977, some of which were reasonably accurate in their information as to why such a defect should occur in vessels often after only two or three years from moulding, whilst others expound some wild and confusing theories.

The Y.B.D.S.A. was asked by various factions of the Yachting Industry (particularly those representing Owners and Brokers) to investigate the matter, discuss it with selected manufacturers of hulls and raw materials and to then produce our findings and present the situation as it is known to exist up to date (mid 1978). The contents of this paper are the product of such investigations over approximately 2 years.

In brief the general causes and effects of underwater blistering of polyester gel coats are as set out below.

The polyester resins of which vessels are commonly constructed are to some extent water permeable. That is to say that molecular particles of water will pass through but will not be contained in the resin and hence no appreciable increase in weight or moisture content will occur. Resin manufacturers will usually give data for cast resin samples tested under laboratory conditions and this will usually give results better than 1% weight increase over many months of immersion, so why problems with moulded hulls?

Laboratory conditions can seldom be reproduced in the moulding shop and so various factors come into play that tend to reduce the ideal state of resins. Almost all of these factors tend to make the resin more permeable and perhaps water absorbent also. Let us consider the more general factors encountered.

1. The Degree of Resin Cure

A resin that is not fully cured will be more permeable and hence more prone to defect.

Insufficient curing can arise due to many factors but generally from—

(a) Too low mould shop temperatures, especially in the early stages.

(b) Too high humidity in workshop.

(c) Incorrect catalyst content. This is a common problem as even now some moulders adjust resin gelling time by altering the catalyst amounts beyond the limits of the manufacturers recommendations.

(d) Removing the mould from satisfactory mould shop conditions to poor conditions for the necessary post-curing period. Often from mould shop to adjacent open air parking space as soon as released from the mould. Obviously more of a problem in the winter months especially when hulls are left to collect rain water, snow, etc.

Certain catalysts can be "stopped" and restarted again and will continue to fully react and so produce a full cure of the resin. However, the catalysts more commonly used are not of this type. If stopped due to unsuitable conditions,

they will "decay" and hence when suitable conditions are restored the resultant amount of reaction has been reduced and so a full cure of the resin is not achieved.
The "tolerant" catalyst is usually slower acting under good cure conditions than that more commonly used and hence is unpopular as a result of increased manufacturing time of a given laminate.

) A gel coat that is too thin may not cure satisfactorily and will be more permeable. It may also be resoftened by the application of the first laminating resin to it. The result being that it wrinkles and detaches from the mould and may allow the first glass fibre reinforcement to penetrate it thereby inducing water penetration by capillarity (see Wicking).

Resin Additives

The most satisfactory resin is one that has the least additives other than catalyst and accelerator to manufacturer's recommended proportions. The addition of colour pigments and any filler (not filler used in repair but that used to give the resin more body) may to some extent increase the tendency to permeability but if used in accordance with the resin manufacturer's recommendations will be of acceptable proportions. Dark blue, red and dark green pigments usually incorporate more plasticiser than other colours and in practice are more likely to blister at an early ta. :

Manufacturing Defects

At time of writing this paper the whole condition of "Osmosis" is often considered, especially if some articles in the popular press are to be believed, as a "manufacturing defect". This puts a very unfair slant on the problem from the careful manufacturers position as we shall see later. It is true to say, however, that certain defects" can be avoided or very greatly reduced by attention to the recommendations of the majority of raw materials suppliers not only as regards use but also the range of materials.

Environment in Service

Osmosis" is more likely to be experienced in fresh water than salt due to the ater difference in the relative density of the liquids on either side of the semi-permeable membrane.

o increase in water temperature induces the condition to occur. This is possibly due to a tendency to soften the gel coat slightly and this in turn increases the permeability. Temperature increase will also cause expansion of any liquid already blister and with a slightly softened gel coat expansion of it will be greater.
rk is in hand on the finer points of "Osmosis" by various chemists and eventually re information as to the precise mechanics of the phenomena will be available.

what then is "Osmosis"?

The dictionary defines "Osmosis" as the property of a fluid of a given density separated by a Semi-Permeable Membrane from a fluid of lower density to draw less dense fluid through this membrane, in order to equalise the densities, thereby not only increasing the higher density fluid's volume but also generating a pressure if no escape behind the membrane exists. Basically, this is how a tree [illegible] water from the roots to the upper branches.

I have seen that polyester resin is to some extent a semi-permeable material. This o problem until one considers that within G.R.P. hull there can be literally millions of small cavities. Even with the most careful control of resin mixtures and applications of mouldshop conditions and of consolidating the laminates, there will be micro cavities. The most common of these will be in the strands of the glass themselves. Glass strands are formed from bundles of glass filaments each of which is considerably thinner than a human hair.

The glass has a binder to hold it all together in the fabric condition as supplied to the moulder but obviously the strands and filaments must be flexible, so micro-cavities exist. Resin is a relatively high viscosity liquid and no amount of hand rolling will cause the resin to absolutely impregnate every micro-cavity.

Also in addition to the above micro-cavities, other cavities in the form of small (and sometimes not so small) quantities of air exist in the overall moulded structure.
We therefore have a structure containing many unavoidable micro-cavities with perhaps a proportion of larger ones also. This structure is to be separated from the water in which it is to live its life by a semi-permeable surface coating, THE GEL COAT.

Water molecules commence to pass through the gel coat as soon as it is immersed. If there was no other factor involved, there would be no problem.

Unfortunately, on finding one of our micro-cavities, the water molecules collect to form droplets and soon the cavity is filled. At this juncture the vessel will in effect have taken on a small amount of extra weight of water.

The chemists become the authority from here on and they inform us that the water begins to react with the resins and glass binders that they are in contact with.
There are often many constituents contained in the liquid found in these cavities but basically the liquid is acid in nature. It also becomes of greater density than the liquid outside and so "Osmosis" is born. The effect is then progressive.

If the "Osmotic" cavity is beyond the glass reinforcement the membrane is strong and can withstand high pressure, the chemists are quite matter of fact about pressure of 5 to 6 atmospheres (75 to 90 p.s.i.) being recorded in deep seated blisters. Hand laid mouldings are basically layers of reinforcement with layers of resin between. The resin is relatively weak and the pressure of 70 to 90 p.s.i. will cause the resin to fracture and the moulding to delaminate. Bigger cavity, more osmosis, etc., until real loss of structural strength occurs.

How to stop this condition taking place?

As far as possible, we must try to keep the water out of our unavoidable cavities; to do this we need a good water barrier, gel coat polyester resin may not be the best material to use but can, if of the best quality possible, give good results, and no other material that can be used in the same way as a gel coat in the moulding process.

From what we have seen above, the following requirements are recommended if we are to obtain a reasonable service life from a moulding before "Osmosis" occurs.

(a) Careful control of mixing and application of gel coat especially to avoid all air inclusions.

(b) Full cure of the gel coat and rest of moulding to resin manufacturers specifications including post curing time.

(c) Gel coat preferably to be clear and carried to 2" - 3" above designed waterline. This improves permeability and enables a visual inspection so that any areas of air inclusion may be removed.

(d) Gel coat to be of sufficient thickness. This is most important as it has been found that the improvement in permeability is better than directly proportional to any increase in thickness.

Care must also be taken to ensure a gel coat is used that will enable the required thickness to be applied on the structure without subsequent cracking, that is to say a rigid structure will enable a less flexible resin to be used but a flexible structure will require a flexible gel coat to avoid cracking due to flexing. Water passing through cracks is a short cut to deeper "osmosis" within the laminate.

Resin manufacturers currently recommend a cured thickness of clear air free gel beneath the water line to be [illegible] to [illegible] thou of an inch in thickness (0.5 mm to [illegible]).

The writer's experience shows that in many vessels where clear gel coat has been used, thickness is often no more than 8 to 10 thou of an inch and often as little as 5.

Gel coat can easily be measured when applied by the use of a wet film thickness gauge. When measured wet allow 10% for shrinkage on curing. It seems that few moulders use these simple gauges and hence have no real knowledge of what thickness gel is applied. Quantity of resin per boat is no indication as it may be 40 thou of an inch in one place and 5 in another.

Clear gel usually looks much thicker than it is especially under certain lighting conditions.

There are better water barriers than polyester resin and of them, 2 pack polyurethane paint and 2 pack epoxy paint are in general use but mostly as a repair medium.

These paint coatings are referred to in more detail later in this paper.

all blisters are as a result of true osmosis

tioned above is cracking of underwater gel coat as a short cut to "osmosis"
n the laminate. Another common short cut is prominent fibre, sometimes called
king". Due to the ends of many strands of glass protruding through the gel coat
sing so close to the surface that the gel cracks and so water is drawn into the
nate by capillarity effect. Osmosis is to some extent usually present. Also, this
t has been more common in recent months in the writer's experience where
r gel had been used.

rs found during survey vary greatly but basically are usually of the following
:—

Gel coat void blisters

This is where the gel coat has had various bubbles trapped or generated in it at manufacture, the condition is commonly termed "Aero Chocolate Gel Coat" for obvious reasons. These blisters appear as relatively small (1/8" diameter or less) circular mounds usually in groups and generally containing a liquid which is acidic and has a noticeable aroma.

Usually such conditions give rise to true osmosis from bubble to bubble, until the underlying laminate is reached. Often the distance from laminate to outer surface of gel coat will exceed 20 thous of an inch but void inclusion may exceed 50% of the volume.

Prominent Fibre or Wicking

This is where the fibres either penetrate the gel or are only covered by perhaps 5 thous of an inch at most of gel coat. These blisters are usually elongated with random alignment corresponding to the direction of the underlying glass strands, close examination shows them often to be "almond" shape with pointed end where the strand of glass is closest to the surface.

Water penetrates the strands by capillarity and can go from strand to strand deep into the laminate depending on quality of laminate consolidation (wetting out). Although the water passing along the capillarities does not build up an osmotic pressure, where thin resin barriers are encountered local osmosis can occur.

(c) Interface Blisters

These occur where a change in the permeability of the resin layers occurs, usually where gel coat meets lay up resin and/or where first and second gel coat applications meet. It is now an acceptable practice to double gel moulding and if the resin manufacturers' recommendations are adhered to in respect of degree of cure of the first application, no problem should arise. However from examination of laminate sections it appears that the first layer of gel can cure out too much and the next layer does not form a good chemical bond, a similar condition can exist between gel coat and first lay up resin. This effect can be increased by additives in the gel coat designed to improve the surface of the resin, i.e. waxes, etc. Air void formation can also exist at the interface.

These blisters can vary in size from say 3 mm diameter upwards and often it is found that the gel can be flaked away adjacent to blistering due to poor bond.

(d) Interlaminate Blisters

These blisters are those that can really effect the structural condition of the laminate. They may arise through true osmosis all the way to an area of "dry matt" or air voids or by means of both osmosis and capillarity, the semi-permeable membrane is now reinforced with the laminate and high pressures can build up within these blisters, 80 to 100 p.s.i. having been recorded. Where relatively large capillarity paths exist, the pressure will be relieved but if the paths become blocked or are of small extent, the osmotic pressure will continue to build up. The process of hand lay up G.R.P. as we have seen results roughly in alternate layers of resin and reinforcement, the resin is relatively weak and it will give way under high pressure resulting in an increase in the area of osmotic cavity and weakening of the structure. Temporarily the pressure may be lessened but as osmosis continues it will build up again.

These blisters are usually from say, 25 mm diameter upwards and may be irregular in shape in the larger sizes, when hit with a small hammer they will not shatter and when pierced usually a liquid will spurt out depending on its viscosity and the diameter of the piercing hole.

Care should be taken to protect the eyes when dealing with these blisters. Removing the outer wall of the blister will indicate the amount of glass reinforcement present and hence depth into laminate. The writer has found such blisters beneath 6 ozs. of CSM Plus gel coat.

(e) Freshwater Blisters

As has been indicated, osmosis will usually occur earlier in fresh water than in salt water. The majority of the writer's experience has been with vessels in salt water but the general pattern of blister causes are common to both. What is noticeable is that with the exception of wicking, all other conditions seem to give rise to fewer but larger blisters more randomly spaced. The chemists are looking into the reasons for this. Such blisters can often be seen within a fresh water tank where the inside surfaces are gel coated.

Having described in general terms types of blistering most commonly found in the writer's experience and the apparent most obvious causes for their existence, we must turn our attention to what the implications of this defect are for the owner of a vessel and for the yachting industry as a whole.

The writer has formed the opinion that the manufacturers of both raw materials and of complete mouldings were not aware of the extent of the problem, a common percentage quoted by such sources is as little as 1% to 2% of all boats moulded and reaching an age of five years or so.

Over the past two years, the writer's general experience and that of some other surveyors is that approximately 15% to 20% of G.R.P. boats surveyed exhibit blistering to some degree, this may well only be 1% to 2% of all those manufactured but is a large number of vessels, approximately 20 to 25 in a years surveying for the writer and similar for the other surveyors interviewed.

The age of vessels exhibiting blistering varies from 9 months to 10 years, the boats that blistered early in their lives were found generally to have very aerated gel coats or prominent fibre due to extremely thin gel coats. In a few cases, vessels 10 years old only exhibited minor blistering usually found to be at the interface of gel coat and underlying laminate.

An opinion has recently been put forward by the manufacturers of some resin that at some time in a vessel's life blistered gel coat beneath the water line will be experienced. This has been suspected for some while having accepted that all polyester resins at present in use are permeable to some extent and is generally becoming accepted throughout the industry.

It seems that this eventual condition has to be accepted as is decay in timber and corrosion in metal hulls, also like these traditional materials there are indications that with certain attention to building techniques, coupled with some protective attention, the condition may be alleviated or perhaps prevented altogether. Time is the most necessary factor now required to prove currently suggested methods of both prevention and repair either right or wrong. It should also be borne in mind that since approximately the spring of 1977, the industry as a whole has taken a more active interest in both confirming why blistering occurs and in attempting to suggest ways in which it might be prevented. Some attention is now also being given to treatment of vessels already suffering although the systems of remedial action set out below are those evolved over approximately the past two years by the writer and other surveyors in conjunction with certain paint and raw material manufacturers. It is hoped that with the more active interest in the problem now being shown, even better systems of both manufacture and repair will be evolved in the near future. To this end, Codes of Practice are being drawn up within the industry at time of writing and presumably in the future these will become the works of reference for builders and surveyors alike.

Implications

It is often pointed out (especially by some moulders to whom owners of early blistered vessels have returned) that the gel coat forms NO STRUCTURAL PART OF THE VESSEL. In the areas above water line, it provides a nice surface to look at and saves painting at least for perhaps 5 years depending on the owner's idea of a good yacht finish. In the areas below the water line, it is stated that a gel coat provides a nice smooth finish which enhances the vessel's performance but that otherwise it is generally still as in the topsides, only "cosmetic". When pressed on the point, most moulders will admit that part, if not all, of the function of the gel coat beneath the water line is to KEEP THE WATER OUT OF THE LAMINATE.

Therefore one has to decide on these two conflicting opinions as to the use of the gel coat.

(a) Without a gel coat the vessel would not be structurally weaker as it is a relatively thin non-reinforced layer, therefore without other considerations, it is not of structural consequence.

(b) Without a gel coat beneath the water line and with no other water barrier we have seen that even with very careful wetting out of the fibre glass, water will penetrate the laminate and could then bring about deep seated interlaminar osmotic blistering which could cause more extensive delamination and hence structural weakening of the moulding.

Therefore, in this consideration, the gel coat forms a very important part of the structure in a STRUCTURAL PROTECTIVE ROLE and cannot be dismissed as cosmetic.

From the above, it will be seen that any defect in the gel coat beneath the water line must be considered in the light of the risk of deeper more structural attack on the laminate. This is why surveyors draw special attention to the defect when found, especially if the vessel is under offer of sale. In such circumstances the surveyor is usually asked to give an opinion as to the long term implications of any blisters discovered. Secondary to this usually, is a prospective owner's interest in why the blistering has occured.

So many variables will effect the future course of blistering in a vessel, particularly the quality of laminating of the hull beneath the water line, that a surveyor can only at best make an intelligent guess at both the further extent of blistering, the onset of deeper osmosis and any likelihood of major structural delamination as a result thereof. Two things are certain however, (1) that the condition will not improve with keeping though an opinion as to the rate of further deterioration will be largely guesswork and (2) that the vessel is not going to become structurally dangerous rapidly, this always assuming that the general quality of construction is to good average standard and that we are only at this stage commenting as to gel coat blistering, not deep seated laminate blistering.

Naturally, an intending purchaser does not want to buy a vessel already known to have problems but there is no safeguard that he will find another vessel to his liking which will not either have blistering when surveyed or will not develop blisters very soon after purchase; say one or two seasons or so.

Perhaps two years ago it would be very difficult to sell a vessel that had blisters below the waterline but slowly the yacht buying public have realised that G.R.P. is not the trouble and maintenance free material it was once thought to be and that now many vessels have received remedial treatment with a high degree of success. In the writer's experience, the longest existing repair is coming up to seven years at time of writing with no re-occurence of blisters thus far and the system has hopefully been improved since then.

What now usually happens is that an intending purchaser will complete the purchase provided that the price is adjusted to cover remedial action either immediately or at a time when the blistering is more advanced if found in the very early stage.

If the vessel is not being sold an owner will often leave the condition for a season or two longer, depending on the extent and type of blistering found.

It is the writer's opinion that whilst it is not expected, the deterioration will be rapid or drastic once the gel coat is breached, water has access to the laminate and the onset of deep osmotic blisters could be forming. At best, water may have found its way well into the outer most laminates and can give rise to difficulties when remedial treatment is carried out, therefore it would seem better to carry out remedial action as soon as is convenient.

PREVENTIVE AND REMEDIAL ACTION

(a) Preventive

From the first part of this paper in which are listed the basic forms of "manufacturing" defects, it is obvious that in addition to work shop conditions, curing times, etc., as laid down in the Codes of Practice of the S.B.B.N.F., and Lloyds Register of Yachts, etc., attention must be given to the following:-

(i) Correct mixing and application of the gel coat to the mould, particularly checking the applied thickness with a wet film thickness gauge and the fact that all air bubbles are excluded, the desired thickness being 20 - 22 thous of an inch. It is also essential that if two applications of gel coat are applied, the first is at correct degree of cure when the second is applied.

(ii) As the thicker the resin layer is between the water and first full laminate appears to have a direct effect on the point at which blistering will occur (all other factors being equal). It is currently being recommended that a "full layer of resin be applied immediately after the gel coat" but to prevent cracking, a fine fibreglass reinforcement, e.g. a surfacing tissue or ½oz CSM, should be used. This reinforcement should be thoroughly wetted out but should not be hard rolling which would result in a low resin glass content in this region, thus defeating the object of the greater resin barrier.

ii) Laminating may then proceed as usual with care being taken to fully wet out the laminate both during initial impregnating of the fibreglass and also during rolling out.

It is not uncommon for three [illegible] matts to be pre-wetted on the bench and then laid together in the mould being further coated with resin whilst being rolled out. The writer has noticed air bubbles of relatively large size trapped beneath this lay of reinforcement with great difficulty being experienced in trying to remove them, (rather like chasing bubbles behind wallpaper when paper hanging). The result is often to simply break up the large bubble into smaller ones, the situation becomes more apparent when the laminator is using resin which is approaching its "pot life" time limit.

It would therefore seem worthwhile for moulders to investigate the advisability of applying multiple laminates in view of this tendency to aggravate the problem. General argument against sub-items (ii) and (iii) is in respect of extra time involved in manufacture and this is something that must be debated with the moulders in the industry.

) Recent tests have been carried out by some independent bodies and some raw materials manufacturers. These tests, however, have been largely carried out on small samples in laboratory conditions and usually have been accelerated by immersing the samples in heated water.

Whilst these tests do not necessarily contradict findings in actual vessels, it is the writer's opinion that due to the "real life" time scale involved, they can only act as indicators to what might happen to a vessel over say, a five year period.

No one has yet apparently produced a basic hull moulding incorporating the common "manufacturing" defects and then subjected it to immersion in the natural environment of sea and fresh water.

Obviously such experiment would take perhaps five to ten years to complete, assuming that defects appeared in five years and remedial action schemes were given a further five years to be evaluated.

As far as the writer is aware at this time, no detailed experiments have been carried out in respect of remedial action schemes. What experience has been gained in this respect has been at the cost of the owners of the vessels dealt with. Fortunately, the success rate so far has been encouraging, approximately 80%. Remedial action will be dealt with later in this paper.

From the above experiments carried out, the following points seem to be generally agreed upon:-

(a) Quality of moulding should be as previously described.

(b) Some change in previous specifications of resin, and also the binder used in the fibre glass reinforcement, at least immediately after the gel coat, seems desirable.

In consideration of (v) (b) it now seems generally agreed that isophthalic acid resin gives better results than orthophthalic acid resin (we are not at this point considering catalysts or accelerators) but some experimenters have found that not a lot of difference exists between either under experimental conditions, all other things being equal. This being so, if in doubt at least use isophthalic resin in the outer laminate of the moulding.

Also influencing the permeability of the resin is the catalyst and the accelerator used, both type and quantity vary the results obtained. Cobalt is the common accelerator used and most resins used in yacht mouldings are pre-accelerated so this presents no problem.

A catalyst known as MEKP is commonly used and it has been found that it is IMPERATIVE that it be used completely in accordance with the resin manufacturer's instructions as regard proportion to use to any given quantity of resin, generally 2% catalyst is used.

The writer has observed laminators varying the resin geling time, where work shop conditions were either too cold or too hot to enable a satisfactory geling of the resin to permit manufacture time to proceed as planned, by varying the amount of catalyst. This will have very undesirable effects on the final state of the resin. If resin geling time is a problem, then this must be altered by means of the accelerator and NOT the catalyst. The resin manufacturers should be consulted and their advice adhered to.

As most resins are purchased pre-accelerated, this means using a different resin batch for differing conditions. The increase in production costs are unpopular with the class of manufacturer who will adjust geling time via the catalyst.

The fibres of the reinforcement are held together initially by a binder and without going into technical detail here, basically two types of binder are in common use, Emulsion and Powder type. The emulsion type is at this time more in general use but it is now known that this type breaks down more readily in the presence of water and therefore it is being recommended that powder bound matts be used at least in the reinforcement behind the gel coat.

In summarising section (v). (b) it is generally now considered good practice to use isophthalic resin with carefully controlled MEKP catalyst content and powder bound light weight glass fibre reinforcement at least in the first laminate behind the gel coat.

The result of employing this modified production technique is to provide a longer service life before blistering is encountered.

At this time there is apparently still no evidence that blistering can be avoided completely throughout the service life of the vessel which with sensible maintenance is likely to be in excess of 30 years assuming good construction.

(vi) The question arises that if the moulding is going to blister anyhow, why bother with complicated and probably more expensive manufacturing techniques?

What other form of action can be taken?

Obviously a water barrier must be provided for the laminate and if it cannot be incorporated successfully or economically at time of moulding then it must be applied thereafter.

The natural choice of such a barrier would be a paint coating of some sort, it must be easy to apply, be compatible with the polyester resin gel coat and above all should be far less permeable than the polyester gel coat.

Due to the weathering of gel coat surfaces above the waterline through age and the effects of sunlight, certain paint manufacturers developed the use of two pack polyurethane paint coatings which were proclaimed to be more durable and weather resistant than the polyester gel coat. This being so it was inferred that these paints were far less permeable than the polyester resin over which they were used, there was also available two pack epoxy paint coatings which in various forms had been used as underwater protection on steel vessels.

Enquiries put to the paint manufacturers indicated that both of these paints were considered to be roughly (and in non-scientific terms) six times less permeable than the polyester resin in good condition and of same thickness.

Initially, these paint coatings were used in the remedial treatment of vessels that already had problems but in the past year following consultations with the paint manufacturers the writer and some other surveyors have recommended owners of new vessels and certain older vessels where as yet no sign of blistering is evident to apply either one of these paint coatings.

Advisability of this recommendation seems to be confirmed by the writer's experience of identical vessels having been launched within a week or so of each other and lying in the same water exhibiting after some three to five years very different underwater gel coat conditions, some vessels had been painted with an epoxy primer beneath the anti-fouling whilst others had either not been primed or more likely had been etched primed, in no case did the epoxy painted vessels show blistering whilst in several of the others, blistering was evident. Thought was also given to the use of etch primers having contributed to the onset of blistering but this was not conclusive, as vessels which had not been etched also blistered at about the same rate for similar gel coats defects.

Local sample tests revealed that in most cases the epoxy primed vessels had gel coats of thickness and condition much the same as their sister ships so it was concluded that the epoxy paint presented a much better water barrier than the polyester gel coat. This was finally borne out on one vessel which, due to floating below her designed waterline aft, had blistering of the submerged topside above the waterline which was not present below the waterline where the epoxy primer had been used, the vessel had a white gel coat of approximately 10 thous of an inch in thickness where tested above and below the waterline.

In the light of this evidence and bearing in mind the claimed ratio of permeability to thickness of the gel coat versus paint coating the writer suggests the following paint scheme could be applied to all new and as yet undamaged G.R.P. vessels where an owner felt the need for additional precautions to be taken against water penetration other than those normally afforded by a properly applied gel coat. The paint to be carried some 2" to 3" above the waterline where it can most conveniently become the boot-top if desired.

(a) New hulls should be thoroughly degreased by a proprietary liquid.

(b) New and old hulls following removal of ALL anti-fouling paint, should be well rubbed down. An abrasive of approximately 200 grit should be used preferably dry and by hand or low speed orbital sander to obtain a uniform matt surface finish. Rinse off with fresh water and allow to dry.

(c) (1) Epoxy paint coating. Apply three coats of epoxy two pack paint preferably alternate coats of a different colour to ensure full covering by all coats, the paint is best brush applied and not brushed out too heavily thereby resulting in a total thickness of from 8 - 10 thous of an inch (approximately 3 thou of an inch per coat).

(2) Polyurethane paint coating. Apply minimum of four coats two pack polyurethane paint again alternate coats to be of different colour to ensure full coverage of all coats, this will result in approximately 3 - 4 thou of an inch thickness when applied by brush and not brushed out too fully.

(d) The first coat of any compatible anti-fouling paint to be applied in accordance with the paint manufacturer's recommendations, if these are adhered to it is usual for a good firm bond between last epoxy or polyurethane coat and the anti-fouling to be obtained. When, in the later life of the vessel it may be necessary to remove old anti-fouling without damage to the protective paint coatings beneath, there is now available a paint remover to deal with one but spare the other. Care should be taken to avoid damage to the protective paint coatings by use of scrapers, etc., however should damage occur it is relatively simple to locally repair the protective paint coatings in the usual way.

It will be seen from comparison of (c)(1) with (c)(2) above that a thicker and hence presumably better protective layer is obtained using epoxy paint. Three coats are the minimum considered desirable to avoid the risk of local "pinholing" through successive coatings and thin areas due to local over-brushing, etc.

Four coats are recommended for two pack polyurethane for the same reason but being thinner additional coat ensures a good barrier over all areas.

Although it is not essential to use a gel coat etching primer with two pack polyurethane paint, the paint manufacturer usually recommend it, though suggest that the hull should be at least 6 weeks old to ensure adequate cure of the resin.

The writer has no objections to the application of etch primer to a gel coat that is correctly cured and especially is free from voids. As this happy state is often not available, there is a risk of unpredictable rates of penetration of an etching primer which may give rise to permeability problems at a later date. For this reason, the writer prefers to rely on a moderate mechanical key coupled with some chemical affinity between polyester resin and two pack polyurethane paint.

Etching primer cannot be used with two pack epoxy paint coating due to incompatibility.

The writer would not advise the use of etching primer on an old vessel in any case as the degree of permeability of the apparently undamaged gel coat may be such that undue penetration of the etch primer could result in problems which otherwise might have been avoided, this opinion results from past unhappy experience with such a vessel.

In no other situation could the adage, "prevention is better than cure" be more true than in considering underwater blistering of G.R.P. structures. We have seen above that certain factors during moulding will contribute to a structure being more susceptible to the defect but one must also bear in mind that a moulding shop is not a laboratory and that the man applying the resin to the mould may not be acquainted with the scientific niceities of the material that he is using and also that time, materials and mould shop space is at a severe premium, especially in recent time.

Do we then expect too much of the moulder and his product?

The writer's experience is that manufacturers are now very much on the defensive due mostly to an over enthusiastic popular press stressing that all faults lie with the manufacturer and seeming to imply that he is doing it deliberately. Where it has been possible to gain the confidence of moulders, the writer has found them, through their laminators, to be both interested and co-operative as far as they are able.

The biggest problem is that with the inception of G.R.P. yachts, the buying public generally were given to understand that the material was maintenance free and had no known inherent problems such as decay in timber or corrosion in steel, referred to earlier.

In the majority of cases dealt with by the writer, the vessels have been found to be moulded to what is in his opinion "A GOOD AVERAGE STANDARD OF FIBREGLASS CONSTRUCTION", at least as regards the laminating.

We have seen that no matter how hard the moulders may try, there appears always to be a risk of blistering developing at some time in the vessel's life.

Again, in the writer's opinion, it is considered that an owner should not be faced with the problem within the first five years of the vessel's life unless the moulders are not being careful enough.

It is probably true that the raw materials manufacturers may not yet have decided why polyester resin is so much more permeable than say, two pack epoxy paint, but that does not help the owner of a 30ft yacht facing in excess of £1,000 to £1,500 worth of repairs after five years.

It is therefore the writer's express opinion that until something better is proven to be available, all new and preferably not new but otherwise undamaged vessels, should be painted with two pack epoxy or two pack polyurethane paint and that the moulders should maintain their generally satisfactory standard of production. Painting the bottom is no excuse for sub-standard workmanship beneath.

Two additional points are considered worth mentioning here.

One is that water will enter from either side of a laminate and that often the inner surface of a moulding is poorly finished with exposed glass fibres evident. This being so, thought should be given to providing a reasonably resin rich surface especially in the bilges and perhaps two coats of epoxy paint also.

The other point is that, as far as the writer is aware, the Admiralty do not use gel coats on their Mine Counter Measures vessels, but do coat beneath the waterline with epoxy paint.

(b) Remedial Action

Surveyors will usually arrive on the scene when blistering is already present, occasionally a surveyor may be called upon to inspect a vessel not having signs of "Osmosis" with a view to advising if it is likely to occur. To say the least this is a difficult task although careful observations and some testing may indicate when a vessel's gel coat and immediately underlying laminate have more obvious defects likely to induce the onset of osmosis or underwater penetration at an early date. Testing systems without causing structural damage are very limited and basically consist of the following:-

(i) Microscopic examination of the exposed surface of the gel coat with portable instruments.

(ii) Microscopic measurement of thickness of the gel coat.

(iii) Testing the cured hardness of the gel coat (but here it is essential to know the resin manufacturers expected degree of hardness for the gel coat used).

(iv) General observation of the immediately underlying laminates where clear gel coat and laminating resins are used.

It may not be essential in advanced cases of osmotic blistering to establish just what started it, but it is essential to establish if osmotic blisters exist within the laminates and also as far as possible the extent of water penetration. It is the writer's experience that the majority of cases of osmotic blistering are due to either a gel coat that is too thin, say below 8 thou of an inch or so, or to a gel coat having a larger proportion of aeration or micro-cavities.

In the case of this latter condition, distance from outside surface of gel coat to inside surface may well exceed 20 thou of an inch but each small and thin wall between successive voids is in effect a very thin gel coat and penetration from one to another is progressive.

Over the past 18 months and following meetings and discussions with various raw materials and paint manufacturers the generally accepted and recommended remedial action is as follows:-

(a) Carefully grit blast or hand grind to remove all underwater gel coat in way of defective areas back to underlying laminate. Where whole bottom is to be treated remove gel coat to 3" above water line.

(b) Wash off surface with high pressure freshwater spray to dissolve salts and contaminates which are likely to be trapped in exposed glass strands.

(c) The laminate should then be further carefully examined for deeper blisters, areas of poorly consolidated laminate, etc., these being ground out and structural repairs effected as necessary.

(d) The vessel to be placed in location where reasonable control of the temperature and humidity can be obtained and where ventilation will allow drying out of the laminates. Periodic inspection will be necessary by someone experienced to ascertain if the laminates are dry enough to commence remedial action.

(e) Two coats of two pack polyurethane or epoxy paint to be applied to the exposed laminate surface being well worked into the roughened surface.

(f) The deeper pits in the surface to be filled with an initial application of a two pack solventless epoxy filler, care being taken to ensure that air is not trapped beneath this filler.

(g) The remaining surfaces of the underwater hull to be coated with the same filler such that at least 25 thous of an inch exists over the high spots of the underlying laminate WHEN THE FINAL FAIRING IS COMPLETED. This is to ensure that all glass strands are adequately covered to guard against wicking.

(h) The faired surfaces then to be painted with four coats of two pack polyurethane or epoxy paint alternate coats to be different colour to ensure full coverage by all coats. Paint should not be brushed out too thinly.

(i) Apply first coat of compatible anti-fouling over last coat of polyurethane within the time prescribed by the manufacturers to obtain a good chemical bond.

Although the use of two pack polyurethane is the system initially evolved and now in general use, it is likely that the use of two pack epoxy will supercede this. At time of writing, one paint manufacturer is suggesting a system combining the two products but principally resulting in the use of epoxy paint.

It is true to say that at this time no one will give a 100% guarantee against the possibility of some re-occurrence of blistering in a vessel repaired using the above system, but experience shows that if care is exercised at the crucial stages, there is perhaps a better than 80% chance that it will be successful. Time is of course the true test but results with vessels treated as far back as 1971 are encouraging. Some further testing of systems which are hoped to be an improvement on the above system is being carried out at this time, but it is felt that a reasonable period of time should elapse before modifying what is a reasonably satisfactory and reasonably accepted system of repair.

One thing which has now come to light through trying to short cut the above repair system is that once osmosis is established in either the gel coat or the underlying laminate there is no virtue in simply over-coating the surface with polyurethane or epoxy paint nor in removing and re-applying another gel coat. It is really an all or nothing situation if reasonable success is to be achieved. Some cases of apparent success have been cited where "one coat of paint stopped the problem", but where explored further the condition was probably not osmosis as we have described it.

POSSIBLE VARIATIONS OF REMEDIAL ACTION FOR THE FUTURE

Two main deficiencies exist in applying the above remedial action (a) degree of water and/or contaminants left in the laminate and accurate judgement of when dry enough to commence repair (b) ensuring that sufficient thickness of fillers are applied over the fibreglass reinforcemnt to avoid "wicking" problems at a later date.

Considering (a). Initially it was not considered desirable to pressure wash the bared laminate surface as this might drive even more water into the laminates. However following some incidents of reblistering from beneath the paint coatings and fillers applied during repair and the fact that some vessels seemed to be dry one day and damp patches showed the next, it was thought that perhaps salt and other contaminants might be lodged in the glass fibres close to the surface, not only would the salt be incompatible with the paint coatings but would also draw in moisture on a damp day hence the variable patches whilst waiting to dry out.

Samples removed from beneath the reblistered areas again contained salts and contaminants and under microscopic examination these seem to have collected without the overlying coatings being penetrated. It was therefore assumed, hopefully correctly, that they had been there all the time and as the areas were local, only local re-repair was carried out having well fresh water washed the areas and the problem has not re-occurred.

Even with freshwater washing, a great deal of heart searching is required before the decision is taken to repair, this usually results in an arbitrary period of from 3 to 6 weeks between washing off and applying the first coat of paint to the laminate assuming that the vessel has been placed under reasonable cover during this period. Not only does this prevent the owner using the vessel but it slows down the throughput of work and as a large number of vessels are awaiting treatment, the queue gets longer.

There seems to be no good reason for this time lag and it would seem reasonable under conditions of good ventilation, to expect the hull surfaces to be dry enough in 4 to 6 days unless water penetration is very great. The lack of measuring devices greatly aggravates the problem.

The writer has experimented with a moisture cured resin which is claimed to be also tolerant of the contaminants likely to be found in the glass fibres, this resin acts as a primer/sealer over which the two pack epoxy fillers would be applied. So far through lack of sufficient test vessels, results are not conclusive but it is thought that it could be applied soon after freshwater washing and so the remedial work could proceed unhindered.

The other possibility is that some form of moisture content chemical indicator could be utilised, electrical resistance moisture meters as used in the timber trade for instance, have proved to be of no use.

Considering (b). Again, due to re-occurrence of blisters, further investigation revealed that due to insufficient thickness of fillers and paint coatings over the high spots of the fibreglass laminate left following grinding off or grit blasting, some fibreglass strands had penetrated the surface and caused "wicking".

The strands were found to be protruding above the surface by perhaps 10 - 15 thou of an inch. This being so it was decided to call for a minimum of 25 thous of an inch of filler over the high spots before painting. In theory this is fine, but in practice very hard to achieve.

To coat a vessel of say, 30ft - 40ft in length, with perhaps three coats of two pack epoxy filler, fairing up between coats is both arduous and expensive due to labour content and cost of material.

At least one repairer has suggested that basic fairing be done using two pack epoxy filler and thereafter 25 thous of an inch protective coating be built up by successive coats of two pack epoxy paint at approximately 3 thous of an inch per coat. This while seeming to be also a monumental task is far easier than using two pack fillers. It is claimed to be only little more costly on materials and much less so on the labour content.

This system has been discussed with two pack epoxy manufacturers and it would appear that as long as sufficient time is allowed between successive coats to avoid a solvent build up, no problem should exist. A reasonable rate of application is 1 coat per 24 hours.

On the one vessel so far dealt with in this way, microscopic test thicknesses indicated a satisfactory consistency of epoxy coating thickness over the underlying laminate and base fillers. The vessel has gone out to the Middle East and it is hoped that progress reports on the condition of the bottom will be made from time to time.

If the system proves successful, it may well help to speed up remedial action and to keep repair costs to a minimum, presumably eight coats of two pack epoxy should render the vessel almost totally water resistant, assuming that the problems in section (a) above were avoided.

CONCLUSION

In preparing this paper, the writer has expressed [illegible], findings and opinions which he has gathered on this problem primarily over the past 2 years. These opinions could not have been formed without the [illegible] co-operation of certain raw material manufacturers, moulders, repairers and last but by no means least, some owners, brokers and surveyors. The object of the paper has been to pull together all the various strings which seem to radiate from this problem.

During the compilation of this paper, various halts have had to be made in the light of more definite comment being made by various factions within the industry and it is hoped that a continuance of co-operation and interchange of information will be forthcoming as there are still avenues to explore.

It has also become apparent that underwater blistering of gel coat is generally world-wide, both as regards use and production of vessels and that at time of writing it would seem that no one has come up with the full answers but it may be that the British Yacht Building Industry can take their lead in preventing the continuance of this problem.

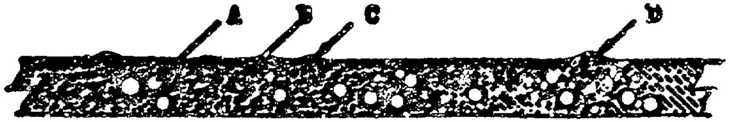
There is obviously more work to be done at a level beyond the capabilities of the writer and it is hoped that a full sharing of both the problems and possible solutions to them will be entered into.

ALAN C. OLFORD

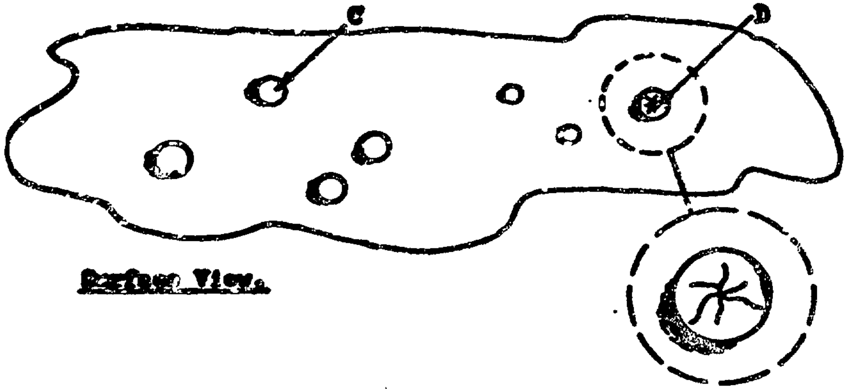
November 1978

Reprinted 1980

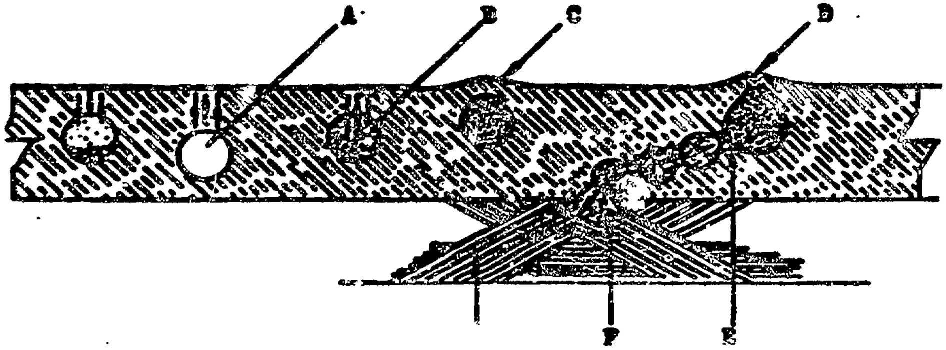
This paper is not intended to be a Code of Practice. Discussions still proceed between manufacturers and surveyors and there is as yet no universal acceptance of a single set of principles to be followed. It should not be assumed automatically that any one who departed from any of the recommendations in this booklet had thereby adopted an inferior method, or had laid himself open to a complaint of negligence or of failure to produce a product which was of merchantable quality.



Section thro' Gel Coat.



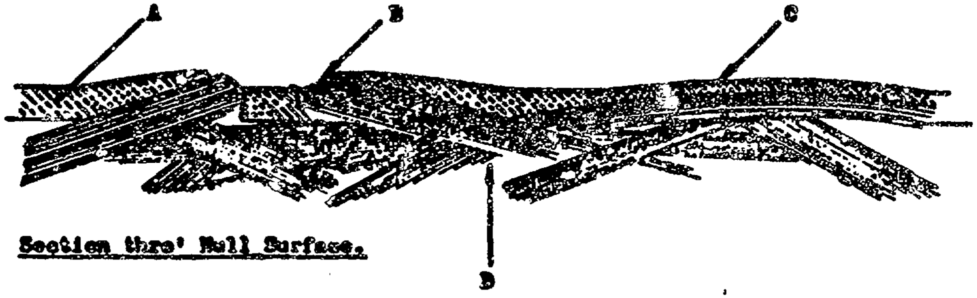
Surface View.



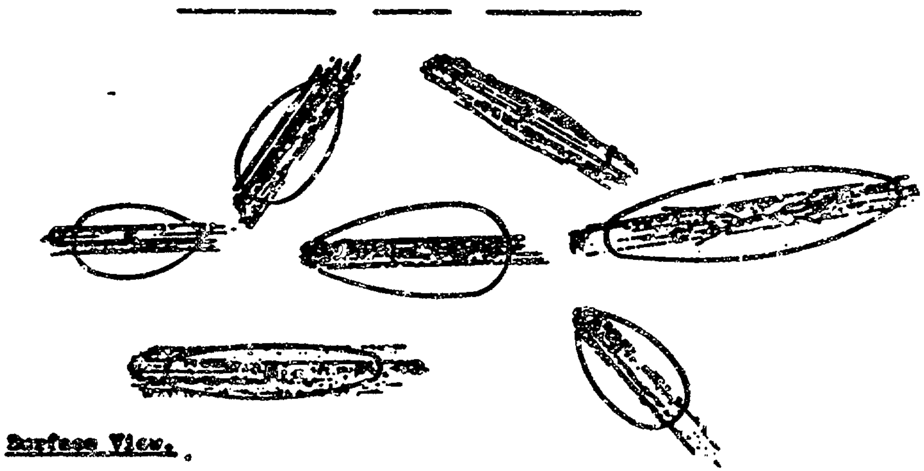
- **A** Air void or inclusion.
- **B** Liquid filled void at neutral pressure.
- **C** Liquid filled void under osmotic pressure distorts gel coat.
- **D** Gel coat ruptures and releases pressure.
- **E** Adjacent void subjected to moisture penetration. Stages A to D take place but rupture of void wall at higher pressure.
- **F** Progressive penetration of moisture from void to void until laminate is reached.
- **G** Laminate.

"AERATED" GEL COAT giving rise to OSMOSIS

ACO/OS 1



Section thro' Hull Surface.

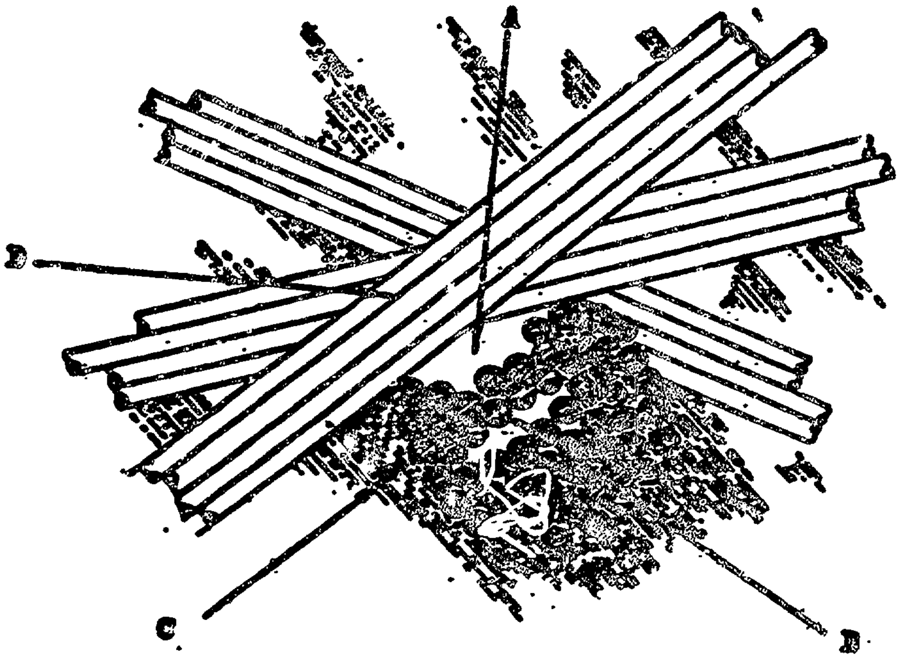


Surface View.

- **A** Gel coat very thin or non-existent over fibres.
- **B** Ends of fibres penetrate gel coat surface giving characteristic almond shape blister.
- **C** Moisture in fibre close beneath surface causing distortion of gel coat. If osmotic pressure present, gel coat ruptures.
- **D** Laminate into which moisture has direct access.
- **E** Blisters aligned with fibres.

PROMINENT FIBRE or "WICKING" giving rise to OSMOSIS

ACO/OS 2



A Void at fibre cross over.

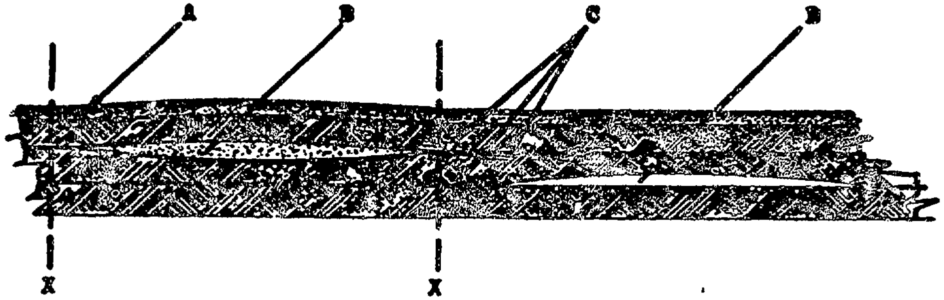
B Voids formed in glass strand bundle.

C Laminate resin.

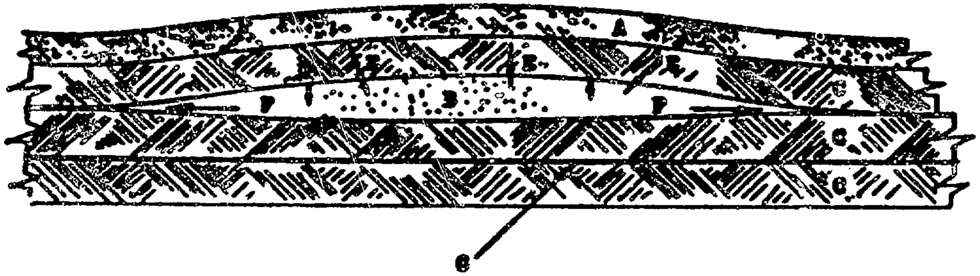
D Random fibres.

"MICRO-VOIDS" in laminate. Diagrammatic.

ACO/OS 3



Section thro' laminate.



Enlargement X-X.

A Permeated gel coat distorted under pressure.

B Liquid filled inter-laminate void.

C Laminates.

D Inter-laminate air void.

E Moisture penetrates laminate to fill void.

F Osmotic pressure tends to rupture resin bond between laminates and distorts thinnest laminate.

G Resin rich layer between laminates with little or no fibre reinforcement between laminates.

INTER-LAMINAR VOIDS and OSMOSIS

ACO/OS 4

Blister performance of GRP systems in aqueous enviro XXXI s

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Abstract

Prolonged and continuous contact with water can, in some cases, cause blister formation in glass fibre reinforced polyester laminates; this paper discusses the results of an independent study of blister formation in various GRP systems after continuous contact with distilled water at 40°C – a condition estimated to give an acceleration factor of 5 to 6 times compared with the same environment at 23°C. In addition to discussing the effects of gel-coat surface tissue, resin type and glass type, it is hoped that the work at present in progress will be satisfactorily completed so that the influence of additives, such as pigments, and other reinforcement systems can be described.

The paper does not set out to explain the mechanism of blister formation nor is it implied that the systems discussed will totally eliminate the problem. Experimentally it has been shown that some glass-resin systems will delay the onset of blistering for considerably longer periods than others. Improvements can generally be obtained for a modest cost penalty either in terms of increased materials cost or increased fabrication time but in some instances materials showing improved blister performance are unlikely to be acceptable to the industry because of their difficult handling characteristics in hand laminating situations.

In practice there are examples where some GRP systems have resulted in blister formation and yet there are countless other examples where similar systems have given no problems. It is concluded, therefore, that blister formation cannot be attributed to one single parameter but to a combination of parameters, such as inadequate protection of the laminate, incorrect choice of material for the environment, poor cure, unacceptable void content and dry patches, and in some instances a contribution from the user himself – incorrect choice and use of etch primers before applying antifouling agents.

1. Introduction

Blistering in GRP structures, which are continuously immersed in water has been given much publicity in recent years and yet we know of only 4 publications on the level of the problem. Platell (1) reports an incidence, in Australia, of more than 10% of swimming pools showing the effects of blistering in less than two years. Taylor (2) and Olford (3) express concern over the instances of blistering but do not quantify the level of the problem, although in 1973 (4) it was estimated that 5% of boats and 4–5% of pools blistered in the U.K. If these are reasonable estimates then there is indeed a need to find acceptable solutions to the problem of blister formation in GRP.

Examples of blisters in GRP components are shown in Figure 1. They form by a process known as "osmosis" and in the last few years more has been written about blister formation in GRP than at any other time since its introduction into the marine industry, more than twenty-five years ago. Various aspects of the phenomenon discussed in the literature are described in the Appendix.

Blister formation is a complex process which is affected to a greater or lesser extent by the type and thickness of gel-coats, the type of resin, additives, the type of reinforcement, the laminate construction, manufacturing defects and service environment. Quite often, but least suspected, damage can be caused by the use of etch primers before applying antifouling agents. The GRP industry was offered recommendations in 1973 (4), supported by experimental evidence, which would reduce the risk of blistering in GRP components. Unfortunately these recommendations together with those published by McInnes (5) of Lloyds Register of Shipping and the BPF Recommendations (6, 7) have not been implemented by the industry.

The work discussed in this paper was carried out by an independent test house (Kunststoffen en Rubber Instituut TNO in Holland) at the request of Scott Bader Company Limited and Fibreglass Limited. TNO was chosen as the test house because of their expertise in this area of research, having previously carried out studies for other European materials suppliers. This work showed that imperfections such as, air inclusions – either air bubbles or in glass fibre bundles; poorly impregnated areas in the reinforcement; micro cracks; and places where there is poor interlaminar adhesion, can initiate blistering (8).

The aim of the programme was to determine which GRP systems were most resistant to blister formation and hence to provide practical suggestions for laminating. The programme discussed in this paper was divided into two phases: –

Phase 1: involved a study of the effects of various clear gelcoats, resin types, surface veil, and glass mat types on blister formation. Data obtained from this phase of the work was presented at a symposium in 1979 (9, 10).

Phase 2: involved a study of the effects of additives, such as pigments, other reinforcements and mixed glass systems on blister formation.

2. Experimental

2.1 Raw materials

The following raw materials were used to construct the laminates: –

(a) **Polyester Resins**

- (i) Isophthalic gelcoat: –
  - Type I – based on a medium heat deflection temperature (HDT) isophthalic resin;
  - Type II – based on a medium HDT isophthalic-neopentyl glycol (NPG) resin;
  - Type III – based on a low HDT isophthalic resin.
- (ii) Orthophthalic back-up resin (medium HDT marine resin).
- (iii) Isophthalic back-up resin: –
  - Type I – medium HDT marine resin.
  - Type II – high HDT marine resin

(b) **Reinforcement:**

(i) 300g/m² and 450g/m² emulsion bonded chopped strand mat (CSM):–
  Type I – fast "wet-out";
  Type II – slow "wet-out".

(ii) 300g/m² and 450g/m² powder bonded CSM:–
  Type I – using polyvinyl acetate (PVA) sized filaments;
  Type II – using resin sized filaments.

(iii) Surface tissue – "C" glass type.

(iv) 600g/m² balanced woven roving.

(c) **Ancillary Materials**

(i) Deep blue pigment.

(ii) White pigment.

(iii) Methyl ethyl ketone peroxide (MEKP) catalyst.

2.2 Laminate Construction

The Guidance Notes (6) issued by the BPF were used as a reference for the construction of the laminates. They were laid up on a Formica surface at a temperature between 20 and 22°C, and a relative humidity (RH) between 46% and 61%. Gelcoat, when used was applied by brush (700g/m² ∼ 0.5mm thick layer). The gelcoat was allowed to cure to a 'tacky' state before the back-up layer of surface tissue and/or 300g/m² CSM was laid down. This was allowed to cure to a rubber-like state before completing the laminate with 3 X 450g/m² chopped strand mat or woven roving/CSM composite (600, 450, 600g/m²). Each laminate was consolidated with a metal roller.

A resin:glass ratio of 2.25:1 was used for the CSM and 1:1 for the woven roving as recommended by the BPF guidelines. A resin to glass ratio of 20:1 was used for the surface tissue.

2.3 Cure and Post Cure Conditions

Throughout the project 2% MEKP was used with the pre-accelerated resins except when the effect of catalyst concentration was being assessed.

Phase 1 laminates were post-cured as follows:–

Half as specified by the BPF guidelines (24 hours at 20°C on the mould followed by 16 hours at 40°C) and half for 28 days at 20°C.

Phase 2 laminates were all post-cured according to the BPF guidelines.

2.4 Method of Immersion

Circular specimens 11.5cm in diameter were cut from the laminates and clamped at the ends of tubes with screw-on caps and rubber gaskets (see *Figure 2*) to provide liquid tight seals.

The vessels were then loaded with lead weights and floated on water such that 75% of one surface of the laminate was in contact with distilled water at 40°C. Each vessel contained two ventilation ports to prevent excessive build-up of water vapour in contact with the other surface since the experiment was set up to study single sided contact conditions. Six floating vessels were placed in each water tank and maintained at temperature in air circulating ovens at a relative humidity below 40%.

2.5 Method of Assessing Blister Formation

Samples were visually examined every 2 weeks during the first 6 months and thereafter every 4 weeks. Blister formation was judged using the following assessment scheme:–

Type 1 = Fibre whitening, no blisters.
Type 2 = As 1 but with small blisters, or small blister only.
Type 3 = As 2 but some of the blisters (diameter 1–2mm) had burst.
Type 4 = As 3 but some blisters (diameter 3–4mm) had also burst.
Type 5 = Some blisters diameter 4–5mm appear.
Type 6 = Start of formation of blisters diameter >5mm.
Type 7 = Extension of 6.
Type 8 = Blisters form with diameter >10mm.

The higher the mark the more serious the blister formation.

Examples of each blister type are shown in Figures 3–6. No samples exhibited type 8 blisters within the duration of the experiment.

Specimen examination was always carried out by two independent workers and their assessment combined and averaged. At the end of the exposure period all the samples were photographed.

2.6 The Programme

All GRP systems examined in the Phase 1 (duration 12 months) are summarised in Table 1. Laminates were made in duplicate and post-cured as described earlier.

42 systems were evaluated in Phase 1 – using duplicate specimens, 2 cure systems, and 4 immersion periods (i.e. 3, 6, 9 and 12 months) – a total number of 672 specimens were immersed in water.

The systems evaluated in Phase 2 are shown in Table 2; 32 systems were evaluated; this involved the immersion of 128 specimens.

3. RESULTS AND DISCUSSION

The results of this investigation have been evaluated in terms of the effects of the individual components before considering how they interacted within the total GRP system.

3.1 The Gelcoat

The data shown in Tables 3 and 4 show that the use of gelcoats significantly prolongs the time to onset of blister formation and in many systems their use prevented blister formation within the time scale of the work.

The isophthalic-NPG gelcoat system shows some advantages over the basic isophthalic gelcoat system. The influence of gelcoat on blister formation over the complete Phase 1 work is illustrated in Figure 7. Here the influence of glass type and surface tissue have been ignored and clearly an advantage is gained by using an isophthalic-NPG gelcoat especially in conjunction with an orthophthalic back-up resin system. Table 5 compares white and clear gelcoated systems and confirms that white gelcoats in general give equivalent performance to clear gelcoats. This was not unexpected because the white gelcoat systems used here contain pigment paste dispersed in the gelcoat base resin system and not in low molecular weight carrier media which are more susceptible to hydrolysis and likely to give inferior resistance to blister formation. The reason for the poor performance of the deep blue gelcoat (see Table 4) must be associated with the pigment carrier medium for reasons explained above. It is also obvious from Tables 5 and 6 that the isophthalic Type I gelcoat is more resistant to blistering than the isophthalic Type III gelcoat. This is a function of the base resin system; the latter gelcoat being based on a resin of lower HDT performs less well under the 40°C immersion test conditions.

3.2 The Surface Tissue

A resin rich layer associated with the use of a surface tissue gives improved blister resistance in all cases compared with the same system without surface tissue, as shown in Tables 3 and 4. The advantages of using a surface tissue are also illustrated in Figure 8 independent of glass type and resin type.

3.3 The Laminating Resin

The laminating resins investigated in the programme were a marine medium HDT orthophthalic acid based resin and two marine isophthalic acid based resins, one with a medium HDT and the other with a higher HDT. The data obtained for these systems are shown in Tables 3 and 4 for the various laminate constructions. The isophthalic acid based laminating resins generally outperform orthophthalic acid based resins. The performance of each resin is shown independently of glass type, gelcoat type and surface tissue in Figure 9.

Isophthalic acid based resins show better resistance to blistering than orthophthalic acid based systems; this is a function of their molecular make-up and the ease with which the ester linkage is accessable to water and possible hydrolysis. This has been recognised as a major contributing factor for many years and form as the basis for the current BPF recommendations (6). Isophthalic-NPG resins have even better resistance than the basic isophthalic systems (11, 12), again as a result of steric effects. This is the main reason for isophthalic-NPG gelcoats giving better performance.

Even if an isophthalic acid based resin is not used throughout the construction advantages can be gained by using this type of resin at least in the first few millimetres of "lay-up" and has been recommended as a reasonable compromise (5, 6).

3.4 Reinforcements

Figure 10 shows the effect of different types of CSM on GRP systems without gelcoat and independent of back-up resin type. Figure 11 shows similar curves for gelcoated systems. Where no gelcoat is used there is little difference between the emulsion bonded mat (EB) Type I, and powder bonded mat (PB), Type I. Powder bonded mat, Type II does give better performance but is considered unsuitable for hand lay-up because handling and air release difficulties can be encountered when fabricating large and complicated structures. However, where a gelcoat is used, Tables 3 and 4 show that generally PB mat (Type I) gave a better performance than EB mat (Type I). This is also illustrated in Figure 11.

With the orthophthalic resin, powder bonded mats perform better than emulsion bonded mats except when a neopentyl glycol gelcoat is used (see Table 3), here the emulsion bonded mat system approaches the result obtained with a powder bonded mat. With isophthalic laminating resins emulsion bonded mat can perform as well as powder bonded mat and when used in conjunction with the NPG gelcoat the performance is further improved. The use of a 'C' glass tissue to give an even better resin rich barrier results in further improvements for all systems studied.

In general, the use of slow wet-out emulsion bonded mats gives comparable results to fast wet-out emulsion bonded mats (see Table 7).

Table 8 suggests that where woven roving is used in conjunction with PB mat (Type I) the presence of the woven roving has no observed effect on blistering. Insufficient data was obtained from the programme to draw conclusions from the EB mat (Type I)/WR systems.

In orthophthalic resin systems, a single layer of PB mat behind the gelcoat gives some improvement in blister resistance (see Table 9). However, little improvement is realised by this practice when using the isophthalic resin system.

(i) There are no significant improvements in using a 16 hours at 40°C post-cure compared with 28 days at RT (9).

(ii) Changes in catalyst concentration, 1% to 2% of MEKP had no affect on the rate of blister formation as shown in Table 10.

4. CONCLUSIONS

(i) It is important to consider the performance of the total laminate system since blister formation cannot be attributed to one single factor, but to a combination of factors: – inadequate protection of the laminate, incorrect material selection, poor cure, poor fabrication (especially dry patches) and incorrect use of surface treatments such as etch primers.

(ii) The acceleration factor for the work reported here must also be taken into account. For single sided immersion conditions in distilled water at 40°C compared with the same environment at 23°C an acceleration factor of 5 to 6 has been observed (9). Hence, many of the systems investigated would show no signs of blistering at 23°C for at least 5 years. In fact, seawater conditions at 23°C would undoubtedly result in a greater factor because it is well known that distilled water is the most aggressive medium in which such experiments can be carried out.

(iii) Type 2 blisters, used in this work to describe the onset of blister formations, would not put the mechanical performance of the laminate at risk.

(iv) The incidence of blistering in GRP can be greatly reduced by adopting the following procedures: –

- Use isophthalic gelcoats, especially those based on NPG (clear or white), below the waterline.
- Do not use deeply coloured gelcoats below the waterline.
- Use a surface tissue in addition to a gelcoat.
- Use resins which are less susceptible to hydrolysis, such as isophthalic acid based systems.
- Use reinforcement containing non-hydrolysable binder, especially with orthophthalic based resin systems. This is less important with isophthalic based systems.
- Ensure complete wet-out of the reinforcement together with minimal void content.

(v) The guidelines given in the BPF document (6) provide a good basis for delaying the onset of blistering. This work supports and reinforces many of the recommendations made in the BPF document.

APPENDIX

Various aspects of the blistering phenomenon have been discussed in the literature. A summary of the major points are given here: –

(i) Blisters occur in laminates after long-term, uninterrupted immersion in water with a variable time scale of months to years (8, 11, 12, 13).

(ii) Blisters occur immediately behind the gelcoat or behind the initial layer of glass as a result of air voids at interfaces within the laminate (11, 12, 13).

(iii) The presence of a surface tissue immediately behind the gelcoat reduces the chance of blistering (14) as does a thick gelcoat (8, 13).

(iv) Osmosis causes blisters to expand – a function of the semi-permeable resin-rich surface (11, 12, 13, 14).

(v) Edwards (15) suggested that to achieve blister resistance there is a need to use a gelcoat with a low permeability rate for water. Its permeability should be equivalent or lower than that of the laminate to prevent the build-up of water in voids at the interface – the first requirement for the osmotic process to occur.

(vi) Blisters contain a mixture of low molecular weight substances dissolved in water. The liquid reacts acidically (11, 13). The liquid composition is acetic acid, small quantities of other acids and glycols, metallic ions, products associated with catalysts and accelerators, plasticisers and reaction products of glass fibre coatings (11, 13).

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This paper is not intended as a code of practice, and neither Fibreglass Limited nor Scott Bader Company Limited give any warranty that following any particular course of action referred to in this document will reduce or eliminate blistering. Its purpose is to inform interested parties of results obtained from a programme of work sponsored by Fibreglass Limited and Scott Bader Company Limited.

GRP Systems Evaluated in Phase 1

System	Gelcoat (clear)		Surface Tissue	Laminating Resin			Reinforcement Chopped Strand Mat		
	Type I (isophthalic)	Type II (iso-NPG)	"C"-type	Ortho-phthalic	Isophthalic		Emulsion Bonded (EB)	Powder Bonded (PB)	
					Type I	Type II	Type I	Type I	Type II
1	-	-	X	X	-	-	X	-	-
2	-	-	X	X	-	-	-	X	-
3	-	-	X	X	-	-	-	-	X
4	-	-	-	X	-	-	X	-	-
5	-	-	-	X	-	-	-	X	-
6	-	-	-	X	-	-	-	-	X
7	-	-	X	-	X	-	X	-	-
8	-	-	X	-	X	-	-	X	-
9	-	-	X	-	X	-	-	-	X
10	-	-	-	-	X	-	X	-	-
11	-	-	-	-	X	-	-	X	-
12	-	-	-	-	X	-	-	-	X
13	-	-		-	-	X	X	-	-
14	-	-		-	-	X	-	X	-
15	-	-		-	-	X	-	-	X
16	-	-		-	-	X	X	-	-
17	-	-		-	-	X	-	X	-
18	-	-		-	-	X	-	-	X
19	X	-	X	X	-	-	X	-	-
20	X	-	X	X	-	-	-	X	-
21	X	-	X	X	-	-	-	-	X
22	X	-	-	X	-	-	X	-	-
23	X	-	-	X	-	-	-	X	-
24	X	-	-	X	-	-	-	-	X
25	X	-	X	-	X	-	X	-	-
26	X	-	X	-	X	-	-	X	-
27	X	-	X	-	X	-	-	-	X
28	X	-	-	-	X	-	X	-	-
29	X	-	-	-	X	-	-	X	-
30	X	-	-	-	X	-	-	-	X
31	-	X	X	X	-	-	X	-	-
32	-	X	X	X	-	-	-	X	-
33	-	X	X	X	-	-	-	-	X
34	-	X	-	X	-	-	X	-	-
35	-	X	-	X	-	-	-	X	-
36	-	X	-	X	-	-	-	-	X
37	-	X	X	-	X	-	X	-	-
38	-	X	X	-	X	-	-	X	-
39	-	X	X	-	X	-	-	-	X
40	-	X	-	-	X	-	X	-	-
41	-	X	-	-	X	-	-	X	-
42	-	X	-	-	X	-	-	-	X

TABLE [illegible]

GRP Systems Evaluated in Phase 2

System	Gelcoat			Surface Tissue	Laminating Resin			Reinforcement			
	Type I (isophthalic)				Orthophthalic	Isophthalic		WR	WR	FB	FB
	Clear	White	Blue			Type I	Type II	Type I	Type II	Type I	Type I + WR Type I
1	X	-	-	X	-	X	-	-	-	X	-
2	-	X	-	X	X	-	-	X	-	-	-
3	-	X	-	X	-	X	-	X	-	-	-
4	-	X	-	X	X	-	-	-	-	X	-
5	-	X	-	X	-	X	-	-	-	X	-
6	-	-	X	X	-	X	-	-	-	X	-
7	-	X	-	-	X	-	-	X	-	-	-
8	-	X	-	-	-	X	-	X	-	-	-
9	-	X	-	-	X	-	-	-	-	X	-
10	-	X	-	-	-	X	-	-	-	X	-
11	-	-	X	-	-	X	-	-	-	X	-
12	-	X	-	-	X	-	-	-	-	-	X
13	-	X	-	-	-	X	-	-	-	-	X
14	-	X	-	-	X	-	-	-	X	-	-
15	-	X	-	-	-	X	-	-	X	-	-
16	X	-	-	-	-	X	-	-	X	-	-
17*	-	X	-	-	X	-	-	-	-	X	-
18*	-	X	-	-	-	X	-	-	-	X	-
	Type III (isophthalic)										
	Clear	White	Blue								
19	X	-	-	-	-	X	-	X	-	-	-
20	X	-	-	-	-	X	-	-	-	X	-
21	X	-	-	X	X	-	-	X	-	-	-
22	X	-	-	X	-	X	-	X	-	-	-
23	-	X	-	-	-	X	-	-	-	X	-
24	-	-	X	-	-	X	-	-	-	X	-
25	-	-	X	X	-	X	-	-	-	X	-
	Type I (isophthalic)							CSM/WR			
	Clear	White	Blue					Using WR Type I CSM	Using FB Type I CSM		
26	-	X	-	-	X	-	-	X	-		
27	-	X	-	-	-	X	-	X	-		
28	-	X	-	-	-	-	X	X	-		
29	-	X	-	-	X	-	-	-	X		
30	-	X	-	-	-	X	-	-	X		
31	-	X	-	-	-	-	X	-	X		
32	-	X	-	X	-	X	-	-	X		

* - 1% MEKP

TABLE 3

Time in Weeks to Onset of Blistering (Type 2) of Laminates Produced with Orthophthalic Acid Based Resin Systems.

Resin	Clear Gelcoat	'C' Glass Surface Tissue	CSM REINFORCEMENT		
			Emulsion (Liquid) Bonded Mat (Type 1)	Powder Bonded Mat (Type 1)	Powder Bonded Mat (Type II)
Orthophthalic	None	None	7	7	6
	Type I	None	14	[illegible]	42
	Type II	None	35	36	>52
Orthophthalic	None	✓	10	10	51
	Type I	✓	46	>52	>52
	Type II	✓	22	>52	>52

TABLE 4

Time in Weeks to Onset of Blistering (Type 2) of Laminates Produced with Isophthalic Acid Based Resin Systems.

Resin	Clear Gelcoat	'C' Glass Surface Tissue	CSM REINFORCEMENT		
			Emulsion (Liquid) Bonded Mat (Type 1)	Powder Bonded Mat (Type 1)	Powder Bonded Mat (Type II)
Isophthalic (Type 1)	None	None	10	6	7
	Type I	None	30	>52	>52
	Type II	None	>52	>52	>52
Isophthalic (Type 2)	None	✓	>52	42	>52
	Type I	✓	>52	>52	>52
	Type II	✓	>52	>52	>52
Isophthalic (Type II)	None	None	14	7	9
	None	✓	14	[illegible]	>52

TABLE 5

Time in Weeks to Onset of Blistering (Type 2) of Systems Incorporating Clear and White Gelcoats.

Resin	White Gelcoat	'C' Glass Surface Tissue	CSM REINFORCEMENT		Clear Gelcoat	
			Emulsion (Liquid) Bonded Mat (Type 1)	Powder Bonded Mat (Type 1)	EB (Type 1)	PB (Type 1)
Orthophthalic	Type I	✓	42	33	46	[illegible]
Isophthalic (Type 1)	Type I	✓	>52	>52	>52	>52
Orthophthalic	Type I	None	14	[illegible]	14	[illegible]
Isophthalic (Type 2)	Type I	None	44	>52	[illegible]	>52
Isophthalic (Type 1)	Type III	None	No data	[illegible]	No data	No data

TABLE 6

Time in Weeks to Onset of Blistering (Type 2) of Systems Incorporating Clear and Pigmented Gelcoats

Resin	'C' Glass Surface Tissue	CSM	Gelcoat	GELCOAT COLOUR		
				Clear	White	Blue
Isophthalic (Type 1)	✓	[illegible] (Type 1)	Type I	>52	>52	[illegible]
Isophthalic (Type 1)	None	[illegible] (Type 1)	Type I	>52	>52	[illegible]
Isophthalic (Type 1)	None	[illegible] (Type 1)	Type III	15	[illegible]	6
Orthophthalic (Type 1)	✓	[illegible] (Type 1)	Type III	No data	No data	3

TABLE 7

Time in Weeks to Onset of Blistering (Type 2) of Systems Incorporating Dust and Mass Wet Out Emulsion Bonded Chopped Strand Mats.

Resin	White Gelcoat	'C' Glass Surface Tissue	CSM REINFORCEMENT	
			Dust Wet Out Emulsion Bonded Mat (Type I)	Mass Wet Out Emulsion Bonded Mat (Type II)
Orthophthalic	Type I	None	16	[illegible]
Isophthalic (Type 1)	Type I	None	44	[illegible]
Isophthalic (Type 1)	Type I (Blue)	None	30	51

TABLE 8

Time in Weeks to Onset of Blistering (Type 2) of Systems Incorporating Woven Rovings.

Resin	'C' Glass Surface Tissue	White Gelcoat	CSM REINFORCEMENT			
			EB Mat (Type 1) with WR	EB Mat (Type 1) without WR	[illegible] (Type 1) with WR	PB Mat (Type 1) without WR
Orthophthalic	None	Type I	[illegible]	[illegible]	12	14
Isophthalic (Type 1)	None	Type I	>52	>52	14	44
Isophthalic (Type II)	None	Type I	[illegible]	No data	14	No data
Isophthalic (Type 1)	✓	Type I	>52	>52	No data	>52

TABLE 9

Time in Weeks to Onset of Blistering (Type 2) of Systems Incorporating Mixed Emulsion and Powder Bonded CSM Reinforcement.

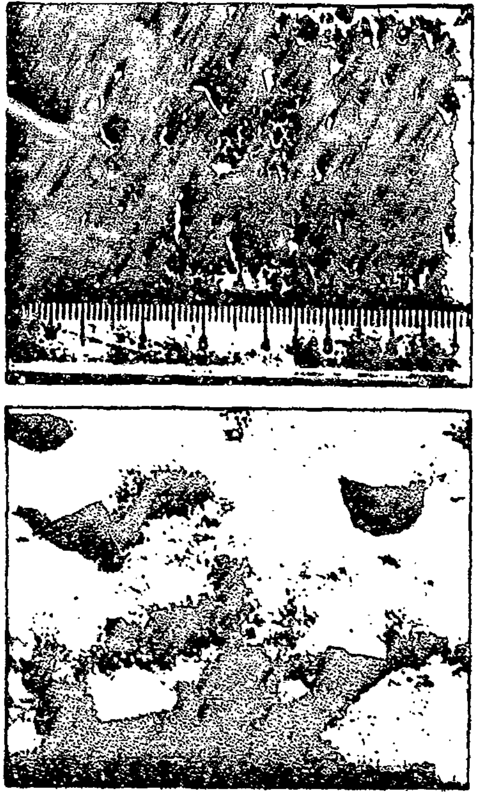
Resin	White Gelcoat	'C' Glass Surface Tissue	CSM REINFORCEMENT		
			EB Mat (Type 1)	PB (Type 1)/EB (Type 1) Mixed Mat System	PB Mat (Type 1)
Orthophthalic	Type I	None	14	[illegible]	[illegible]
Isophthalic (Type 1)	Type I	None	44	>52	>52

TABLE 10

Time in Weeks to Onset of Blistering (Type 2) of Systems Incorporating Different Levels of MEKP Catalyst.

Resin	GELCOAT		'C' Glass Surface Tissue	Type of CSM	CATALYST CONCENTRATION	
	White	Clear			%	%
Orthophthalic	Type I	-	None	EB (Type 1)	[illegible]	[illegible]
Orthophthalic	-	Type I	None	PB (Type 1)	No data	[illegible]
Isophthalic (Type 1)	Type I	-	None	EB (Type 1)	>52	>52
Isophthalic (Type 1)	-	Type I	None	PB (Type 1)	No data	>52

Fig 1 Examples of Blistering in GRP Components



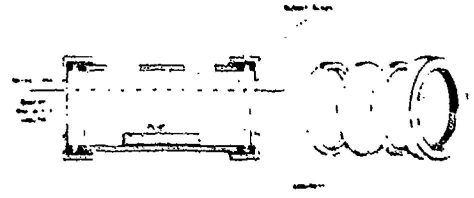
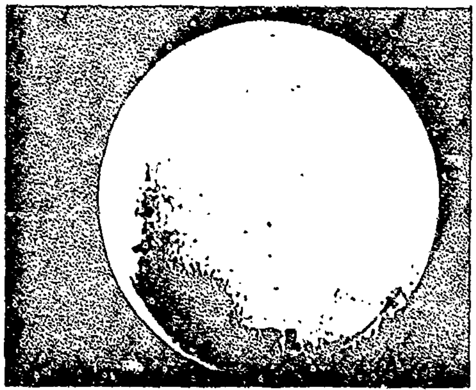
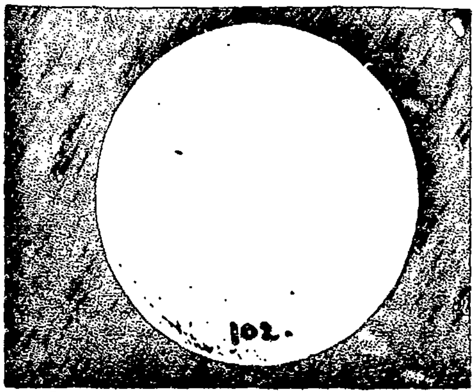


Fig 2 Immersion Apparatus

Fig 3 Blister Assessment (Types 0 and 1)

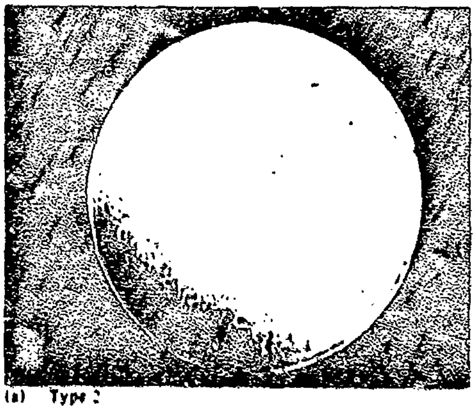


(a) Type 0

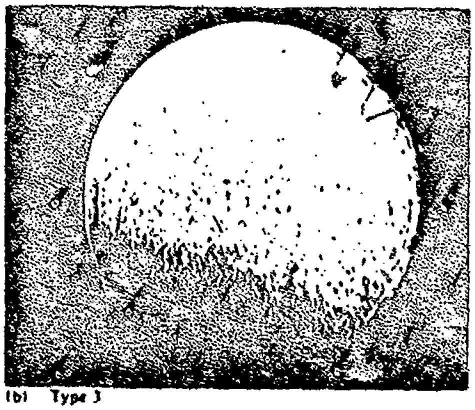


(b) Type 1

Fig 4 Blister Assessment (Types 2 and 3)

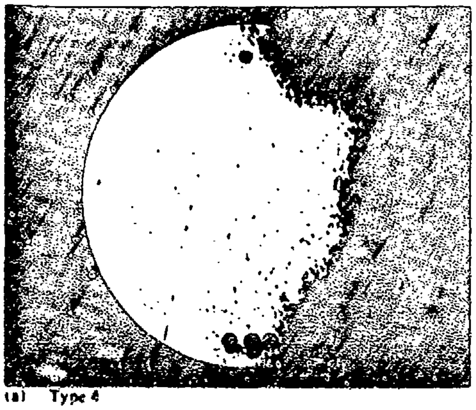


(a) Type 2

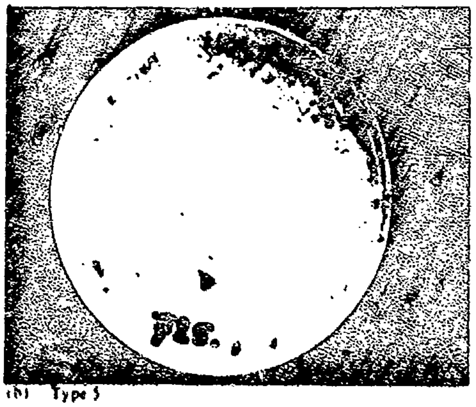


(b) Type 3

Fig 5 Blister Assessment (Types 4 and 5)

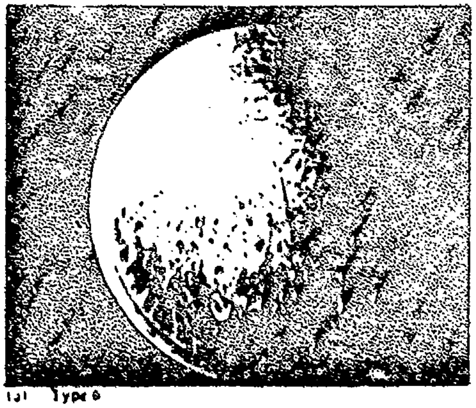


(a) Type 4

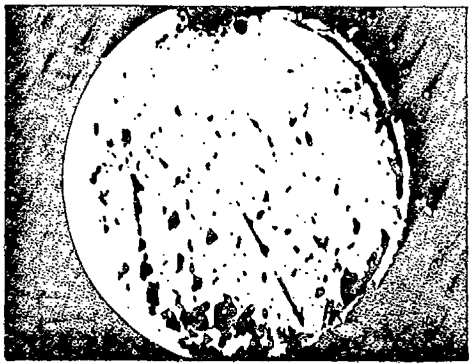


(b) Type 5

Fig 6 Blister Assessment (Types 6 and 7)



(a) Type 6



(b) Type 7

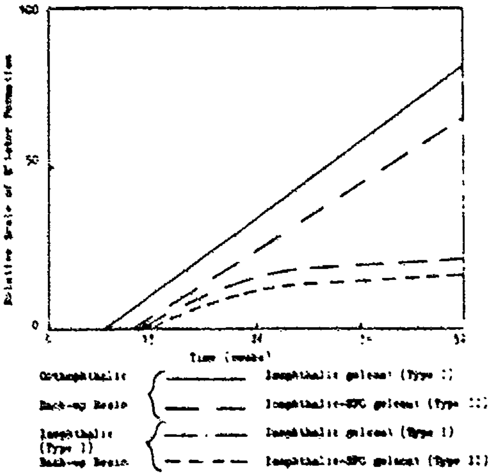


Fig 7 The Effect of Gelcoat and Laminating Resin on Blister Formation in GRP Independent of Other Variables for all Phase 1 Systems

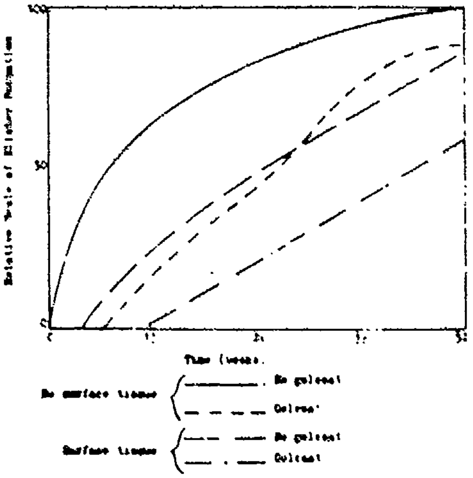


Fig 8 The Effect of Surface Tissue on Blister Formation in GRP Independent of Other Variables for all Phase 1 Systems

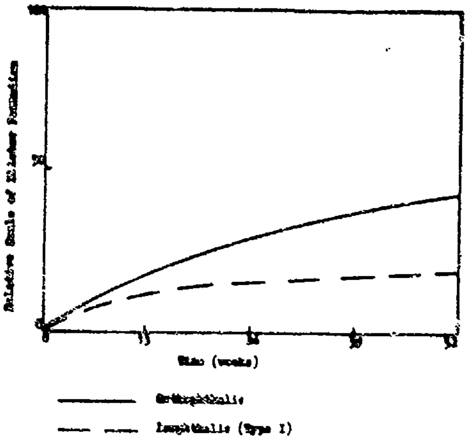


Fig 9 The Effect of Laminating Resin on Blister Formation in GRP Independent of Other Variables for all Phase 1 Systems

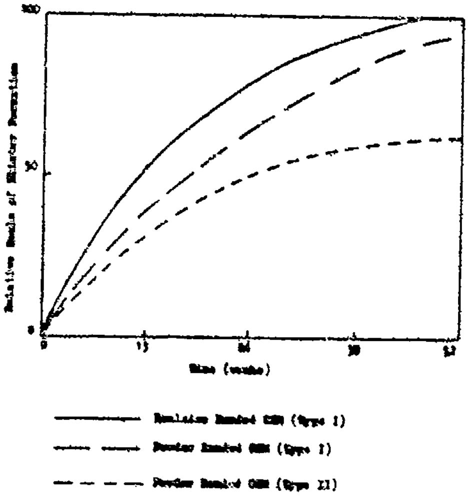


Fig 10 The Effect of Glass Type on Blister Formation in Non-gelcoated GRP Independent of Other Variables for all Phase 1 Systems

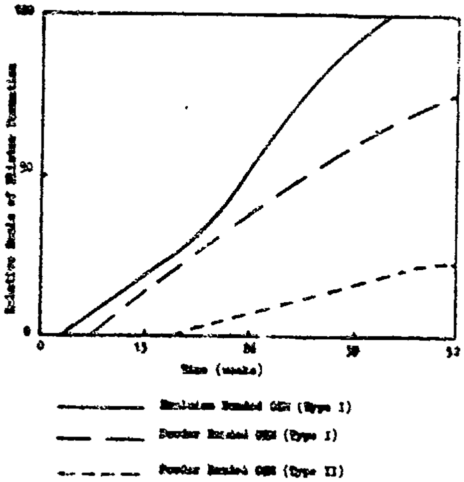


Fig 11 The Effect of Glass Type on Blister Formation in Gelcoated GRP Independent of Other Variables for all Phase 1 Systems

ARTICLE #08-2

C-37

38th Annual Conference, Reinforced Plastics/Composites Institute, The Society of the Plastics Industry, Inc. February 7-11, 1983

BLISTER FORMATION IN RP: THE ORIGIN OF THE OSMOTIC PROCESS

by

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and G. PRITCHARD*

ABSTRACT

Osmotic blistering in polyester-glass laminates is caused by the presence of traces of water-soluble substances in the laminates. These traces can be either substances introduced at the outset, or alternatively hydrolysis products formed later. The analysis of blister fluids shows both kinds of substance present. Notable constituents of the fluids are inorganic cations and certain organic substances, especially glycols. This paper describes results based on the analysis of a large number of laminates using a variety of analytical techniques.

1. INTRODUCTION

The development of blisters between gel coat and back-up laminate in boat hulls and swimming pools has often been noticed, and detailed studies of the subject have been made (1-4). Many of the workers investigating blister formation make recommendations for minimising the problem. There is general agreement that the cause is osmotic pressure, arising from differences between solute concentrations on the two sides of the gel coat. The gel coat acts rather like the classical semi-permeable membrane investigated by Graham, Traube and Pfeffer (5). This paper reports an analysis of the nature of the solutes responsible for generating osmotic pressure, and relates this analysis to comparative rates of blistering.

The mechanism of blister formation is believed to be as follows. When a laminate is exposed to water, there is invariably water permeation through the gel coat, mainly by activated diffusion, but also by microscopic surface cracks or pinholes in the gel coat, arising either from fabrication procedures or subsequent history. The water collects in microvoids or other cavities within the laminate, and slowly fills them. Appreciable quantities of water-soluble substances may be present in the resin, or in other constituents of the laminate at the outset, but even if they are absent, chemical reactions between the water and such constituents as binder, size, glass and resin take place, with the formation of water-soluble substances. Consequently, the region underlying the gel coat eventually contains pockets of concentrated aqueous solutions, and diffusion of more water occurs through the membrane so as to dilute these solutions. Provided the osmotic pressure generated is high enough, the gel coat will either blister or crack, depending on its mechanical properties.

The processes of permeation and of hydrolysis are greatly accelerated at elevated temperatures. This enables studies to be made more conveniently, without waiting for two or three years for blisters to form. However, acceleration of the process should not be carried to excess, as alterations in the prevailing mechanisms could take place. Further acceleration can be achieved by total immersion of laminates in water. This is a departure from practical laminate usage which allows water to permeate into the laminate from both sides, and increases the rate of filling of voids and dry patches. The disadvantage is that observed blister onset times no longer correspond with those seen in service, but the acceleration is similar for all the panels tested, and there is no effect on the qualitative anlaysis of aqueous fluids within the blisters except that the fluids collect, and are diluted, more rapidly.

2. EXPERIMENTAL

About one hundred different types of laminate were produced, all by hand lay-up. Each laminate was about 4 mm thick and measured 914 mm × 305 mm. The reinforcement consisted of four plies of chopped strand mat, impregnated with an orthophthalic polyester resin, and there was an isophthalic, preaccelerated, thixotropic gel coat on one side. Glass content was 28-29% (w/w) and consisted of chopped strand mat of three kinds (all 300 g/m^2):

(1) A PVA emulsion-bound mat with a PVA size.
(2) A polyester powder-bound mat with a PVA size.
(3) A polyester powder-bound mat with a predominantly powder-bound size.

Types 1 and 2 possessed completely identical sizes, coupling agents, and a bundle tex of 102. The third type was treated with the same silanes in a different proportion, and the glass bundle tex was only 51.

The following additional factors were investigated.

(1) Addition of Oxford Blue pigment to the gel coat.
(2) Use of three isophthalic gel coat resins of similar formulation. Gel coat thickness was 0.7 mm.
(3) Use of two mould release agents, one being essentially paraffin wax, the other an aqueous solution of poly vinyl alcohol.
(4) Use of two catalyst/accelerator systems for the lay-up resin; one was methyl ethyl ketone hydroperoxide with cobalt octoate accelerator, the other benzoyl peroxide and dimethyl aniline.
(5) Variations in fabrication procedure.
(6) Alteration of acid value of the lay-up resin.
(7) Addition of free glycol to both the gel coat and the lay-up resins.
(8) Addition of extra dimethyl phthalate to the lay-up resin.

The precise nature of the variations in laminate composition and production procedure will be apparent from the discussion.

All the laminates were allowed to cure at 20 ± 4°C for 24 hours, and postcured at 40°C for 16 hours. They were then cut into smaller pieces and, after storage for periods ranging from 20 to 200 days, most of each variety were painted using eight different painting procedures. Three pieces of each kind of unpainted laminate, measuring 305 mm × 152 mm, were immersed in distilled water, one at 20 ± 4 °C and two at 45 ± 2°C. The painted panels (152 × 101 mm) were immersed at 45 ± 2°C.

The blistering of the painted panels will be reported in a separate publication.

The immersed panel surfaces were examined regularly, and when blisters formed, their nature and sizes were noted. (Blisters were never found on the surface without a gel coat.) The contents of the blisters were removed by hypodermic syringe, and stored in sealed glass ampoules for analysis.

The water in the immersion tanks was analyzed periodically, to determine whether any significant dissolution of cations occurred from the tank walls, the heater/circulators or any other source.

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Gas-liquid chromatography

A Pye 104 instrument was used with a flame ionization detector. A 4 metre stainless steel column, of 3 mm internal diameter, was used with Porapak P-S (a copolymer of styrene and divinyl benzene, silanized) and sometimes with Porapak Q-S (a copolymer of ethyl vinyl benzene and divinyl benzene). Both these stationary phases were supplied by Phase Separations Ltd. Temperature programmed chromatographic analyses were performed and several peaks were assigned by direct seeding (acetone, methyl ethyl ketone, acetic acid, benzene, toluene, the xylene isomers, styrene, ethyl benzene, benzaldehyde and the two glycols used in making the polyester resins, namely propylene glycol and diethylene glycol). No attempt was made to estimate either the less volatile dibasic acids, or the dimethyl phthalate from the catalyst diluent, because their low solubility in water suggests that they could not contribute substantially to osmotic pressure generation. Semi-quantitative analyses were performed for the five major organic compounds found.

Cation analysis

A known volume of each blister fluid was heated with a known volume of concentrated nitric acid (A.R.) to destroy any organic species present, and the residue extracted with dilute hydrochloric acid, followed by analysis for cations using a Corning Model 400 flame photometer, AAG Varian and Perkin-Elmer 370 atomic absorption spectrophotometers. Blanks were performed in each case. Qualitative information was also obtained from an EDAX analyser, coupled to a Cambridge 600 scanning electron microscope.

The water in which each type of glass mat had been refluxed for 7 days was analysed by atomic absorption spectroscopy to determine the extent of cation leaching. Cations in the glass fibres themselves, and in the residues from ignition of some of the resins, including a pigmented one, were detected by the EDAX technique. Quantitative anlaysis of the ash from the lay-up reisn was performed by atomic absorption spectroscopy and flame photometry.

Free glycol analysis

The quantity of free glycol leached from samples of laminate after prolonged storage and then two days' reflux in water was determined by GLC.

3. RESULTS AND DISCUSSION

3.1 General observations

This program involved the immersion of over a thousand panels, and it is not practicable to present all the results obtained in one paper; the effects of painting the laminates will be described elsewhere. This reduces the scope of the present discussion to a few hundred panels.

It should be remembered that throughout the blister growth process, water is entering the blisters and diluting the fluids contained therein. The higher the initial concentration of solutes in the blisters, the greater the initial osmotic pressure, and the faster the dilution occurs. Therefore, at relatively short immersion times, there will be a greater disparity between observed concentrations in various blisters than is detectable later. The time chosen for sampling the blisters had to be late enough for significant sized blisters to have grown in a large number of panels. It was decided that blister fluids would be sampled after about 125 and 240 to 270 days in water at 45°C.

Even so, many laminates did not produce any blisters, or else produced large numbers of very small ones which were very difficult to sample in any quantity.

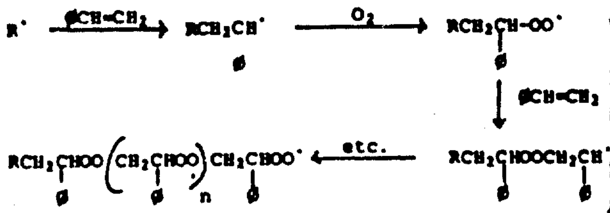
The addition of 2.5% diethylene glycol to the gel coat resin, and 2.5% propylene glycol to the lay-up resin, was carried out in the case of one third of the laminates. This was to observe the effect of free glycol on blistering, since [illegible] often present in polyester resins, and it can be deliberately added to control the viscosity. These laminates containing added glycol were the first to blister, and invariably produced relatively large blisters. The fluids produced could be easily analysed, not only for glycols, but for cations as well. However, the possibility that cation concentraton is increased or decreased by the presence of significant glycol in the blister fluids must be considered.

The blisters in the unpainted laminates formed between gel coat and lay-up laminate. They showed glass fibers underneath, and were sometimes aligned with the fibers (Fig. 1). Some panels had no blisters, some contained many small ones (up to 3 mm diameter) while others contained medium-sized ones (3 to 6 mm diameter). The largest blisters were in excess of 6 mm and relatively uncommon. Fully developed blisters were rather flat in shape, and often contained purple colorations.

3.2 Relative rates of blister formation in unpainted laminates

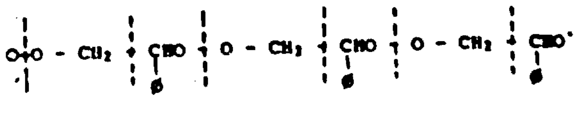
One of the most important factors causing accelerated blister growth was, as stated above, the addition of free glycols to the resins (Fig. 2). This is probably because glycols are water-soluble, whereas dimethyl phthalate, which is present at comparable concentrations as a catalyst diluent, had no such effect. If the water solubility of trace substances is a significant parameter, then acetic acid from the hydrolysis of polyvinyl acetate binder should also encourage blistering. Fig. 3 shows that the emulsion-bound chopped strand mat did produce more blisters, just as it was reported to have done in the investigation by Norwood (1) et al. The finer tex of type 3 glass might have contributed to the improved bliste resistance.

Styrene has a solubility of less than 0.05% by weight i water at 45°C, and should not itself contribute much t osmotic pressure generation. However, in presence of fre radicals (R·) and oxygen, the following series of reactions appear probable (6):



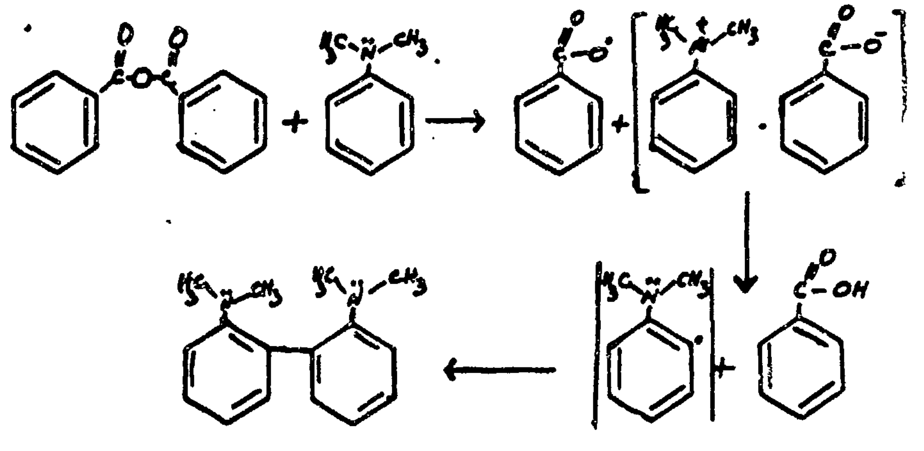
where n = 20 to 30.

The product then decomposes as a result of heat or light t give benzaldehyde and formaldehyde alternately, in a exothermic chain reaction:



Styrene could alternatively be oxidized directly, in th presence of a suitable oxidizing agent, to benzaldehyd benzoic acid, styrene oxide, phenyl glycol or phenyl glyoxal acid (6).

The benzoyl peroxide-dimethylaniline catalyst/accelerat system adversely affected blistering rate (Fig. 4) possibly b producing hydrophilic nitrogen-containing substances an benzoic acid, as shown below:



It should be noted that all the gel-coats were pre-accelerated with cobalt accelerator, and only the lay-up resin was cured with the amine system.

As expected, a lower acid value in the lay-up resin produced an improvement in blister onset time (Fig. 5). This could be because of lower quantities of residual acid and glycol or because of lower hydrolysis and permeation rates. The acid value was about 25 in all cases except those given in Fig. 5.

Addition of Oxford Blue pigment was found to accelerate blistering rate (Fig. 6). The release of water-soluble substances, either from the pigment or from its carrier (1), might be suspected. Direct mixing of solid pigment with the resin, without using a carrier, also produced slightly faster blistering rates.

The effect of fabrication procedure on rate of blistering is a complex question, since several fabrication faults are possible, e.g.

(1) poor impregnation of glass mat, leaving dry patches. NO
(2) Undercure of lay-up or gel coat resin.
(3) Gel coat of uneven thickness, or containing pinholes.
(4) Gel coat gelation time too long, allowing excessive styrene evaporation.
(5) Lay-up resin applied too soon after gel coat application, or too late.

Observations of large numbers of panels made with poor impregnation showed no increase in blistering. If any trend could be observed, the opposite was the case. This might be because the large dry patches could easily absorb all the water diffusing into them without forming a concentrated solution. The laminates made in this way were also prepared with a shorter interval than usual between applying the gel coat and adding the first layer of reinforcement. This did not increase blistering rate.

The possibility of excessive styrene evaporation from the gel coat, before addition of reinforcement, arises from inhibition or retardation of gel coat cure caused by contamination with an inhibitor, by incorrect quantities of excessive surface air-flow or exceptional operating temperatures. One possible cause of cure retardation might be application of the gel coat to a surface made damp by inadequate evaporation of aqueous mould release solutions (7). This is determined by the precise operator technique and workshop temperature, but should not be a problem with wax release agents. Fig. 7 shows that laminates made with paraffin wax were decidedly slower to develop blisters than those made with a polyvinyl alcohol mould release agent. A faulty gel coat could have a higher permeability to water than normal, because of inadequate crosslinking.

The effect of water temperature on blistering rate is shown in Fig. 8. Many laminates which first showed blisters at 45°C in less than 60 days did not show any [illegible] 6 months at ambient temperature. In many other c[illegible]set time was increased. Correlation factors varied from [illegible]out 2 up to nearly 20, making it difficult to predict b[illegible]ring rates at ambient temperatures from the accelerated [illegible]t 45°C.

3.3 Cation analysis

As expected, EDAX examination showe[illegible]e presence of silicon, calcium, potassium, sodium, magnesium and aluminum in the water in which portions of the glass mat itself had been heated in boiling water for seven days. The orthophthalic laminating resin was ashed to produce 3 mg residue from 100 grams of resin, and this residue contained traces of Si, Ca, Mg, S, K, Fe, Co, Cu, Zn, Na, and Ti. On the other hand, a thixotropic isophthalic gel coat produced a much larger residue (2.75%) consisting mainly of silicon, with some magnesium and cobalt traces. Its pigmented equivalent gave 5.4% solid residue, containing silicon and titanium with some chromium, copper magnesium and cobalt. Aluminium was not detected and may have been masked by the silicon.

Quantitative analysis of the ash from the lay-up resin indicated the presence of 100 ppm (based on resin) of sodium, and 3 ppm calcium (by flame photometry) together with 1.5 ppm zinc and 0.2 ppm magnesium (by atomic absorption spectroscopy). Sodium would be expected to escape during ashing and the above figure is therefore low.

The above-mentioned cations released from chopped strand mat after boiling in distilled water of pH 7, were also quantified by flame photometry and atomic absorption spectroscopy. The use of acidic or alkaline water might well have produced larger quantities of cations. The pH of the blister fluids was found to be 4 to 5; Brueggemann reports rather higher acidity (4).

Fig. 9 shows the cation concentrations in a typical blister fluid, after 120 days in distilled water at 45°C. Estimations of calcium made by flame photometry agreed well with those obtained by atomic absorption spectroscopy; the main cations were sodium, potassium, calcium, aluminium, and magnesium. Additional data in table 1 shows the kind of variations between panels. Those laminates containing type 1 glass produced cation concentrations as high as those made with powder-bound mats (types 2 and 3). The improvement in blistering rates (Fig. 3) could be caused by reduced concentrations of acetic acid. However, this question is still undecided (see section 3.4).

Most of the laminates in table 1 contained extra glycol, because laminates of this kind almost invariably produced blisters large enough to supply fluid for atomic absorption analysis.

Ratios of $[Ca^{++}]$ to $[Zn^{++}]$, and of $[Mg^{++}]$ to $[Zn^{++}]$, were very much greater than those found in the lay-up resin, and the majority of the cations Ca^{++}, Mg^{++} and Al^{+++} could only have been extracted from the glass fiber. Iron is present in E-glass but was probably obtained from the immersion heater, and copper could be derived from the copper phthalocyanine pigment.

The magnitude of the calcium concentration alone (Table 1) would be sufficient, if present in the form of a soluble salt, to generate an osmotic pressure of 2 to 5 atmospheres. This pressure would have been much higher at an earlier stage, but falls progressively as the blisters undergo dilution.

3.4 Organic analysis

Organic water-solubles could originate in the resin, the glass treatment (especially the binder), the catalyst, the accelerator, or the diluents in which the catalyst, accelerator and pigment were dispersed.

Fig. 10 shows the principal organic compounds found in a typical blister fluid after 270 days at 45°C. The two glycols were present at higher concentrations than the other major constituents, namely acetic acid, styrene and benzaldehyde. Surprisingly, glycol concentrations were no higher in laminates to which glycol had been deliberately added than in the others, but this can be explained by the fact that dilution rates must be proportional to initial concentration, and so glycol concentrations tend to converge at high immersion times.

The very long retention times gave opportunity for reaction to occur between constituents on the column, especially between acetic acid and glycol. Consequently, the GLC analysis given here is merely an indication of orders of magnitude and could be in error by underestimating some concentrations.

Phthalic and fumaric acid were not estimated, because this would have required the preparation of methyl derivatives. Small concentrations of methyl ethyl ketone were found, possibly from the initiator, and traces of acetone (either from the GLC syringe or the laminating rollers). Various hydrocarbons were identified; many of these were unpolymerizable impurities in styrene monomer (see Fig. 11). Table 2 gives a few examples of the GLC results obtained. Porapak Q-S column packing appeared to give improved glycol stability and higher concentrations than Porapak P-S. Because of the long retention times, the recorder output could not be monitored continuously, and sometimes the glycol peaks went off scale with Porapak Q-S. Osmotic pressure generated from combined glycols was assessed at between one and ten atmospheres at the 125 and 270 days stages. Acetic acid, where present, contributed up to eleven atmospheres, but was not found at all in some laminates, including some emulsion-bound mat laminates. This could again be caused by reaction with other constituents of the blister fluids, either on the column or, more likely, prior to sampling. Blisters from laminates not containing added glycol but showing large quantities of acetic acid tended to appear in the early stages (30 to 50 days) along with glycol-induced blisters.

Addition of extra dimethyl phthalate had no obvious tendency to increase blistering rate. This substance, or other similar phthalates, is used as a catalyst carrier. It has a low water solubility, but could conceivably undergo some hydrolysis to form alcohol. The alcohol would probably be too volatile to remain in the blister fluids for long.

Table 3 shows the GLC analysis of free glycols extracted from the laminates after prolonged storage and then two days' immersion in boiling water. The extra propylene glycol (in those laminates to which it had been added) is clearly evident at about the expected concentration, but the extra diethylene glycol was not apparent. This is explainable by the fact that diethylene glycol was added to the gel coat resin and propylene glycol to the lay-up resin. Therefore the overall percentage of increase in diethylene glycol was small, and its location encouraged diffusion out of the laminate during storage.

4. CONCLUSIONS

The development of blisters between the gel coat and back-up laminate was accompanied by the presence in the laminate of free glycol. A further major factor was the use of an aqueous solution as mould release agent, but this could be countered by allowing generous time for thorough drying of the release film (8). Other factors with lesser influence included the use of a gel coat [illegible] a [illegible] [illegible] agent, and a resin of exceptionally high acid value. The performance of powder-bound chopped strand mat was superior to that of emulsion bound mat.

The concentrations of inorganic cations and of organic substances in the blister fluids have been estimated semi-quantitatively. Several cations were found, and concentrations of up to 0.7% by weight were detected even after nine months of immersion. Calcium was far the most common cation species. The observed concentrations of cations did not depend on glass mat binder.

The main organic substances present were the glycols, benzaldehyde, styrene and (sometimes) acetic acid, but many others were identified at low concentrations.

Complications arose in the analysis of the blister fluids, because of the interaction between the constituents in the blisters before sampling, or during storage in sealed ampoules, or subsequently on the GLC column. Consequently the interpretation of the analytical data and correlation of the data with observed blister development rates, should not be regarded as quantitative.

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BIOGRAPHIES

Geoffrey Pritchard graduated in chemistry, with subsidiary mathematics, from the University of St. Andrews, Scotland. He later obtained a Ph.D. Degree from the University of Aston in Birmingham, England, for a thesis on the cure of unsaturated polyesters. After a period with Dunlop, working on elastomers, he was appointed to Kingston Polytechnic in 1969, and has since concentrated on research into the environmental stability of fiber-reinforced plastics, including graphite fibers, epoxy and phenolic resins and polyesters. He is currently Reader in Polymer Science and Technology at the Polytechnic and is a Fellow of the Royal Society of Chemistry and a member of the Plastics and Rubber Institute.

Joginder Singh Ghotra graduated with honours in chemistry, with subsidiary physics, followed by M.Sc. and Ph.D. degrees from Punjab University, Chaudigarh (India). He came to Great Britain on a Commonwealth Scholarship and worked at Queen Mary College, London, in the area of Metallo-organic Chemistry and Polydiacetylenes. On his return from India after holding a position of Associate Professor of Chemistry, he spent a year at Imperial College, London and later joined Kingston Polytechnic in 1979, where he is a Research Officer in the School of Chemical and Physical Sciences, engaged in the synthesis and evaluation of novel thermosetting resins.

TABLE 1. CATION CONCENTRATIONS IN BLISTER FLUIDS FROM 8 TYPICAL PANELS

Chopped Strand Mat type	No. of days in water	Cation conc. (ppm)				
		Na	K	Ca	Mg	Al
I	240	25	154	4300	650	790
	270	440	570	7500	1850	2850
	120	65	250	2600	565	625
	120	220	225	3750	1250	*
II	270	*	*	1625	375	470
	240	250	175	5875	100	*
	270	15	55	1500	350	425
III	120	*	*	2000	450	575

* Insufficient fluid for analysis

TABLE 2. GAS-LIQUID CHROMATOGRAPHIC ANALYSIS OF BLISTER FLUIDS

STATIONARY PHASE	NO. OF DAYS IN WATER AT 45°C	1,2 PROPYLENE GLYCOL		DIETHYLENE GLYCOL		STYRENE		BENZALDEHYDE		ACETIC ACID	
		Molar Conc. x10^{-2}	O.P.	Molar Conc. x10^{-2}	O.P.	Molar Conc. x10^{-3}	O.P. x10^{-2}	Molar Conc. x10^{-3}	O.P. x10^{-2}	Molar Conc. x10^{-3}	O.P. x10^{-2}
Porapak P-S	125	36.0	9.3	6.6	1.7	1.9	5.0	6.1	16.0	0.8	2.2
	240	36.0	9.3	1.4	0.4	1.9	5.0	5.6	15.0	0	0
	270	35.0	9.3	3.3	0.9	1.8	4.9	6.1	16.0	1.7	4.4
Porapak Q-S	125	*	-	4.5	1.2	2.4	6.2	2.9	7.6	76.0	198.0
	240	*	-	4.3	1.1	9.6	25.0	2.4	6.2	76.0	198.0
	270	3.6	0.9	3.6	0.9	3.7	9.5	3.4	8.9	0	0

* = Peak exceeded chart width

O.P. = Osmotic Pressure in atmospheres

TABLE 3. % w/w GLYCOL (BASED ON LAMINATE WEIGHT) LEACHED FROM 5 TYPICAL PANELS BY BOILING WATER.

GEL COAT*	1,2 PROPYLENE GLYCOL	DIETHYLENE GLYCOL
G_1	0.85	0.85
G_2	0.66 0.40	0.60 0.54
G_2'	2.96 2.30	0.72 0.55

* G_1 = An isophthalic polyester resin.

G_2 = A similar isophthalic polyester resin, from a different manufacturer.

G_2' = The same as G_2 but with 2.5% extra free diethylene glycol added. The difference is not noticeable in this table because the gel coat contributes a very small part of the total laminate weight.

Figure 1. Typical blister between gel coat and back-up laminate. The top of the blister has been cut away to show underlying glass fibers. This laminate contained added glycol. The dark circular grid on the edge of the blister is a 3 mm scale indicator.

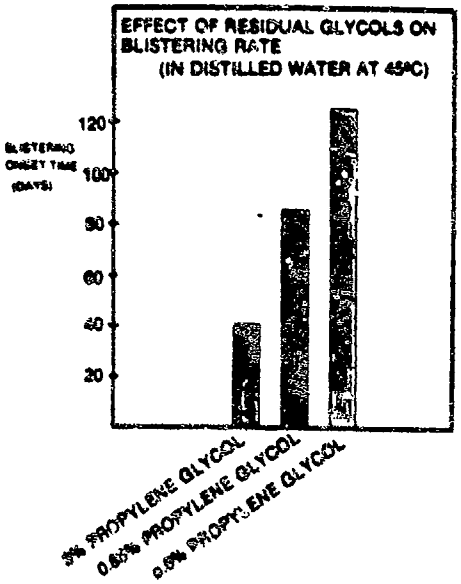
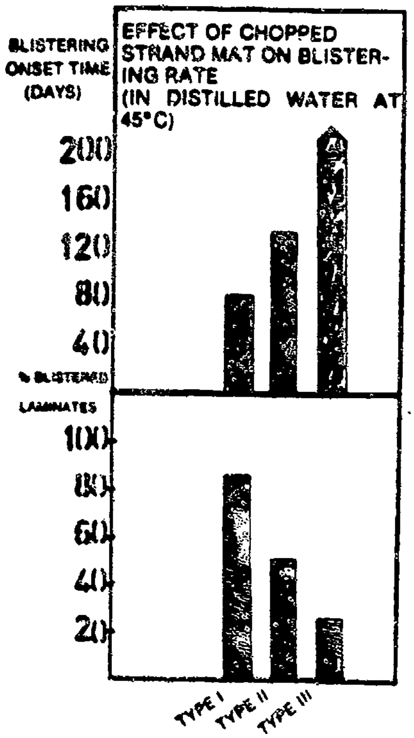
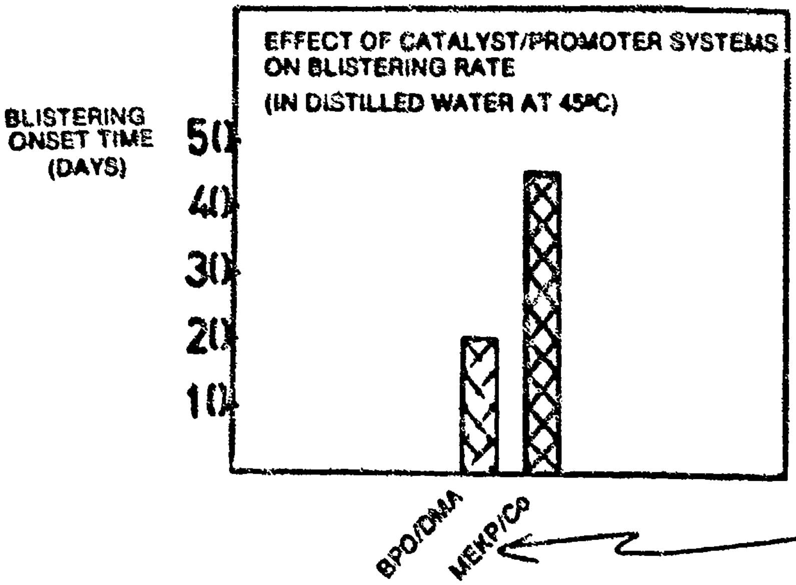


Figure 2. Effect of free glycol concentration on blister onset time (45°C). (Average of ten laminates)



I PVA emulsion-bound mat, PVA size
II Polyester bound mat PVA size
III Polyester bound mat, powder size

Figure 3. Effect of chopped strand mat surface treatment (size and binder) on blister onset time. The treatments are given in the Experimental section of the text. (Average of ten laminates)



NOTE

Figure 4. Comparison of blister onset times obtained using methyl ethyl ketone hydroperoxide/cobalt octoate and benzoyl peroxide/dimethyl-aniline systems. (Average of ten laminates)

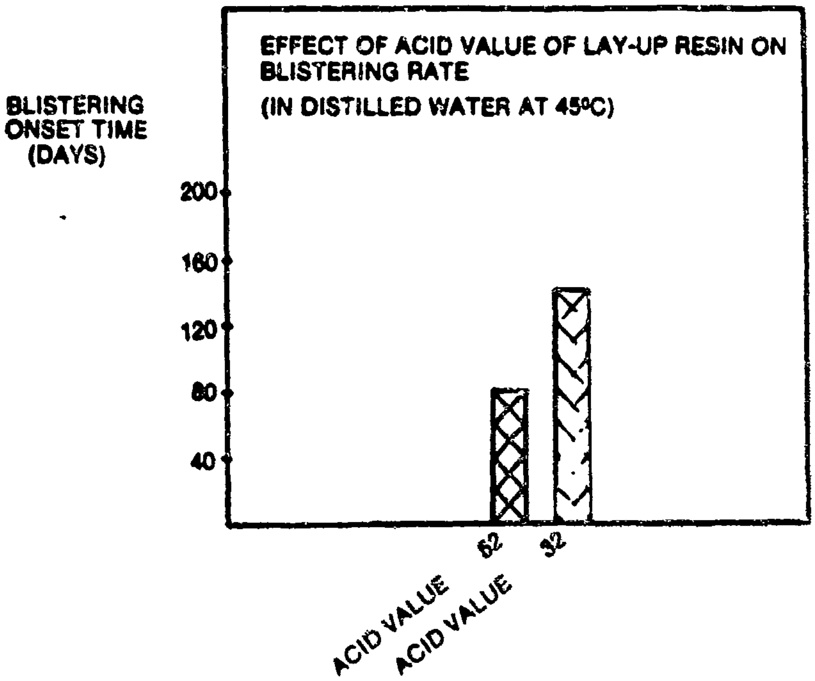
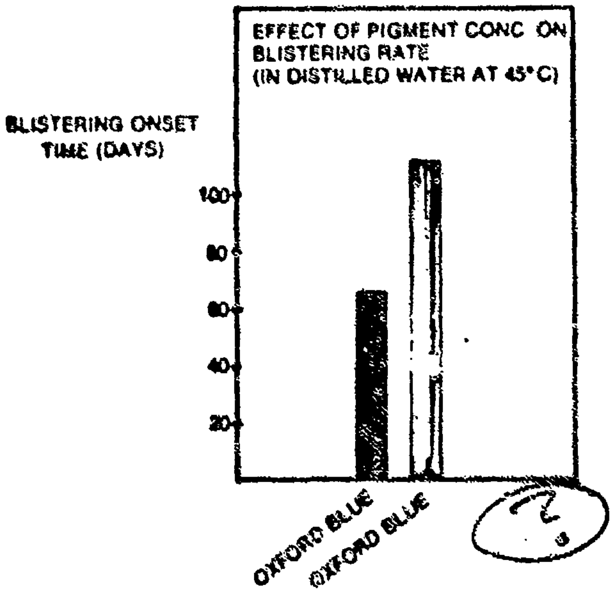


Figure 5. Effect of acid value of lay-up resin on blister onset time. (Average of ten laminates)



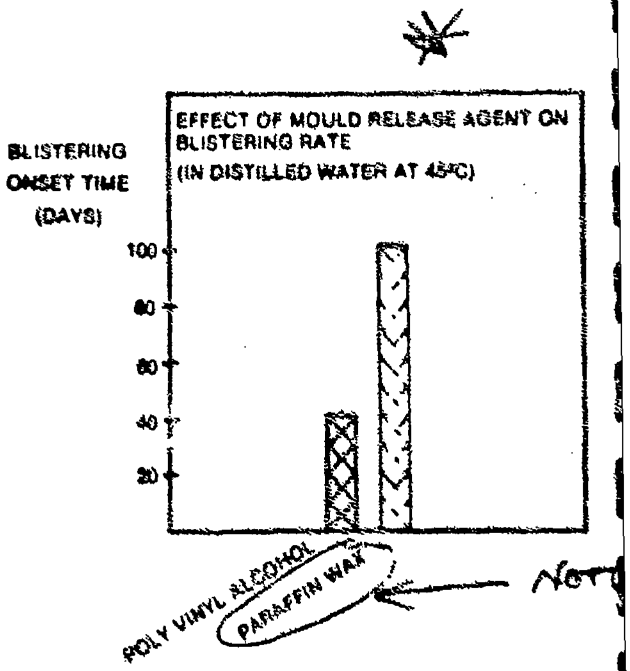


Figure 6. Effect of Oxford Blue pigment in gel coat on blister onset times. (Average of ten laminates).

Fig. 7. Blister onset times with two alternative mould release agents. (Average of ten laminates)

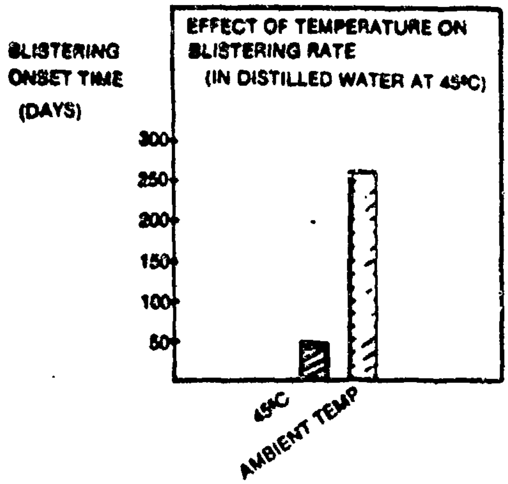


Figure 8. Effect of water temperature on blister onset times. (Average of ten results)

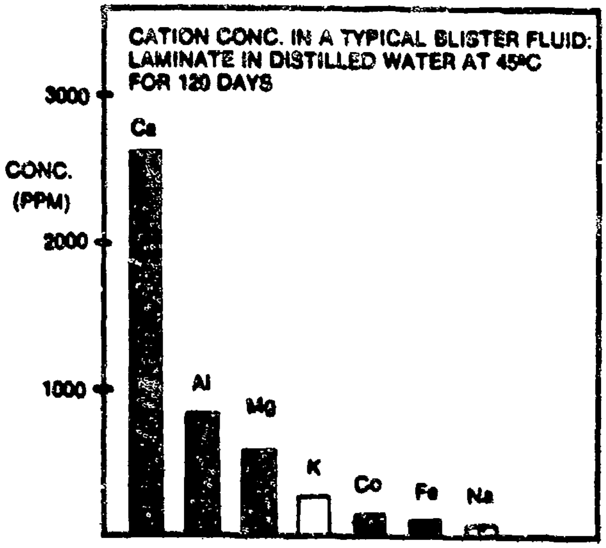


Figure 9. Cation concentrations found in a typical blister fluid after 120 days at 45°C.

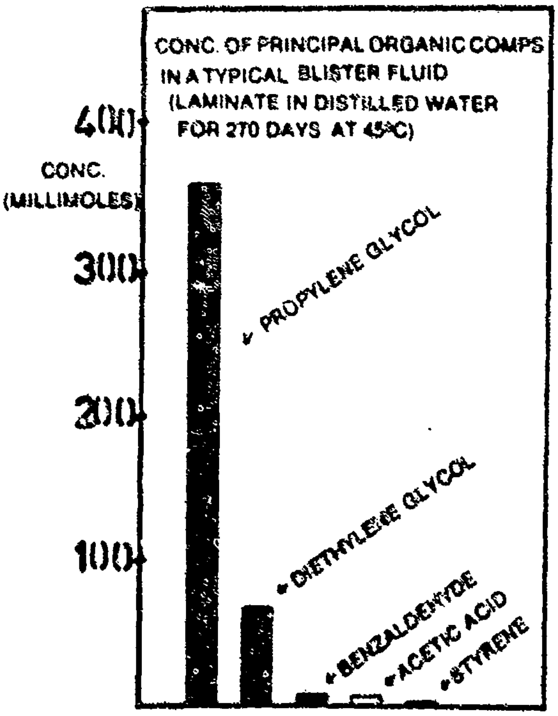


Figure 10. Principal organic compounds found in a typical blister fluid after 270 days in distilled water at 45°C.

APPENDIX D

BIBLIOGRAPHY

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