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**BLISTERING OF GRAPHITE/POLYMER COMPOSITES GALVANICALLY
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**Materials Laboratory, College of Engineering
The University of Rhode Island**

AN ANNUAL REPORT

FOR

Dr. John Sedricks

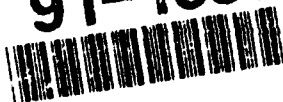
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ABSTRACT

The electrochemical nature of blistering in carbon vinyl ester composites in sea water and saline solution was confirmed. Carbon fiber/polyester composites also blistered. It was therefore shown that blistering is a generic degradation phenomena for many carbon containing polymer composites. The location of the fluid filled blisters in the composites was detailed. The aqueous blister liquid contains organic species and has a pH greater than 10. Blisters formed on vinyl ester/platinum composites caused degradation of the polymer which could not be duplicated in 10N NaOH solution. Absorption kinetics data for water and electrolyte in carbon fiber/vinyl ester composites is established.

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REPORT

INTRODUCTION:

Carbon fibers, being electrically conductive, can lead to a corrosion reaction which poses an entirely new kind of threat to carbon reinforced polymer composites. Carbon is a very noble cathodic material and results in the corrosion of most of the metals that are galvanically coupled to it. This phenomenon is of high probability in sea environments. The galvanic coupling of these composites with metals, besides resulting in metallic corrosion, also was found to degrade the polymer composite itself. The galvanic degradation of the composite is not limited to one polymer system. Tucker and Brown [1] observed blistering of carbon /vinyl ester composites galvanically coupled to steel in seawater. Whereas Donnellan and Cochran [2] studied the galvanic degradation of polyimide composites, Sloan *et al* [3] studied that of the graphite/epoxy composites. A common feature in all these cases was that the degradation occurs under galvanic coupling conditions with high pH blister fluids. A very limited amount of work exists on the galvanic degradation of polymer composites. Although a few mechanisms were speculated, the exact mechanisms of electrochemically driven blistering is not yet completely understood.

The objective of the current research is to conduct analytical and experimental investigations that shall lead to the complete characterization of the electrochemically driven degradation in these composites.

COMPOSITES STUDIED:

The materials worked with during the present study were:

- (1) a Hyfil T 300B carbon fiber reinforced composite with DERAKANE 470-36 vinyl ester as the matrix material. Unidirectional T 300 fibers carbon fiber tows bound together by relatively thin fiberglass wefts were embedded in the vinyl ester matrix in a $[0,90_{11},0]$ lay-up. This material, used in diving equipment and commercially called NOMOADS, is supplied by the Plastechnol, Ltd., Hants, England.
- (2) T 300 carbon fiber/vinyl ester composite with no fiberglass in the reinforcement.
- (3) T 300 carbon fiber/polyester composite.
- (4) Graphite solid disk/vinyl ester composite.
- (5) Platinum/vinyl ester composite.

WATER ABSORPTION KINETICS :

Water absorption behavior of carbon/vinyl ester composites was investigated under uncoupled conditions. These data, on subsequent comparison with absorption data obtained under galvanic coupling conditions, should reveal any electrochemical effects on water transport in these composites. An attempt to study galvanic effects on water pick-up was made by Sloan [4], but the solvent he used was seawater which lead to certain calcareous deposits on the cathodic samples. It made accurate water gain measurements difficult and the changes in water pick-up, if any, were masked out. It was one of the aims of the current project to study the galvanic effects on water pick-up by

using the simple electrolyte, brine solution to simulate seawater. An attempt was already made to collect absorption data under applied potential conditions with 3% NaCl solution as electrolyte, but it did not provide useful results. Efforts in this direction will be continued after refinement of the experimental procedures.

Water diffusion experiments were conducted at 40°C. Diffusion data parallel and normal to the fibers is obtained to account for the anisotropy of the composite. Identical specimens parallel and perpendicular to the fiber layers were cut each with dimensions $(1.25")^2 \times 0.07"$. These very thin samples allow us to reasonably assume unidirectional diffusion through the thickness. The samples were dried in a P_2O_5 desiccator at room temperature. Weight loss during desorption was monitored. The samples took about 20 days to attain a complete dry state. The complete dryness of the samples before absorption experiments is important to determine true water saturation values for the composite.

Absorption studies were conducted for two solvents, namely: pure water and 3% (by wt.) NaCl solution. Data was generated for 5 samples of each category.

The results of the absorption experiments are shown in Figures [1], [2], [3] and [4]. Whereas figures [1] and [2] present diffusion data parallel and transverse to the fibers respectively for pure water, figures [3] and [4] present similar data for 3% NaCl solution. The ordinate in these plots is % weight gain based up on the polymer content of the composite. The curves clearly demonstrate Case I or Fickian diffusion. The absorption curves for neat resin at the same experimental conditions are shown in Figure [5]. It is difficult to conclude whether the sorption behavior of the polymer is Fickian or

ABSORPTION CURVES - PURE WATER

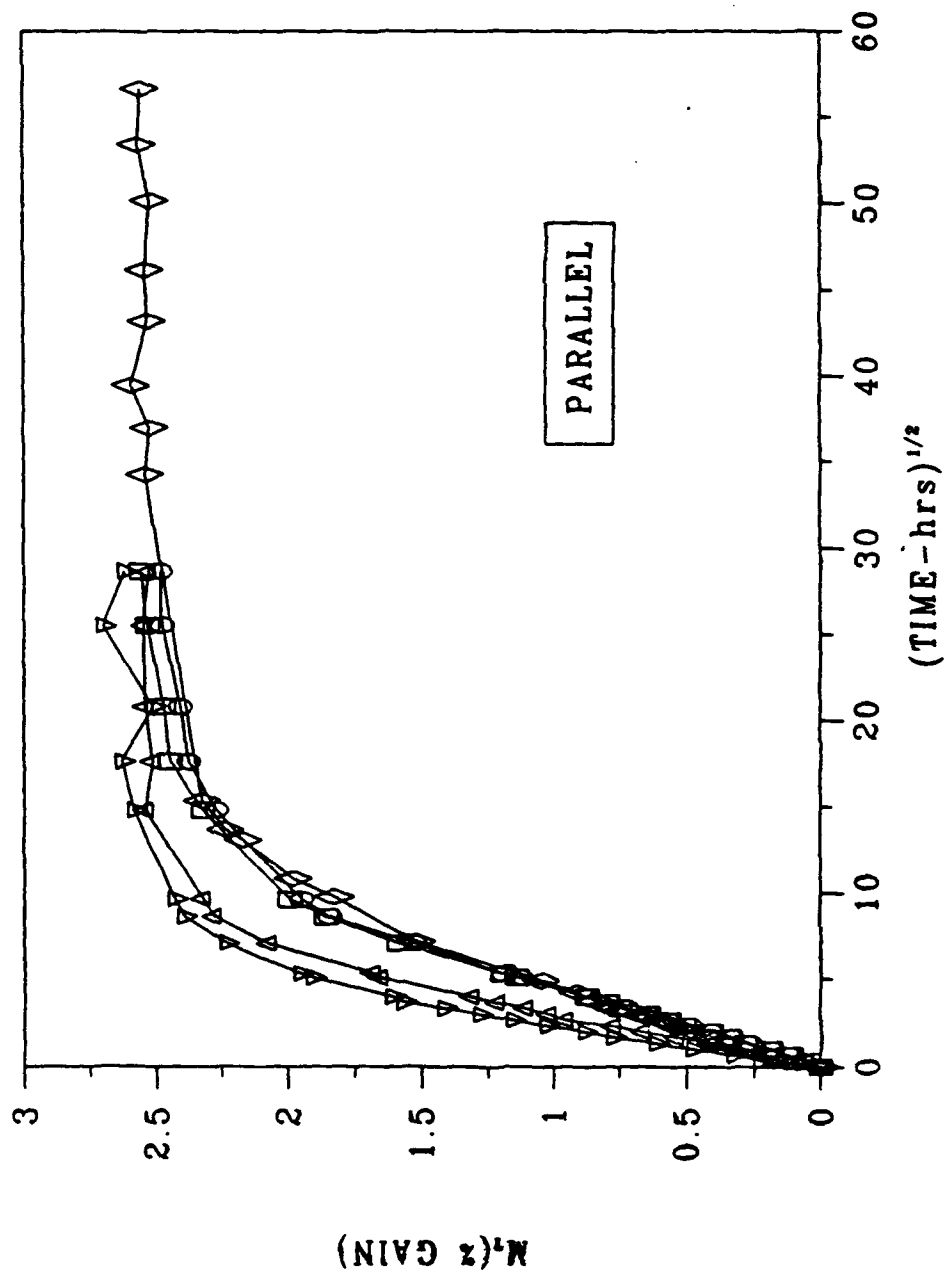


Figure 1. Diffusion curves for pure water absorption parallel to the fibers in carbon/glass/vinyl ester composite. Temperature = 40°C.

ABSORPTION CURVES - PURE WATER

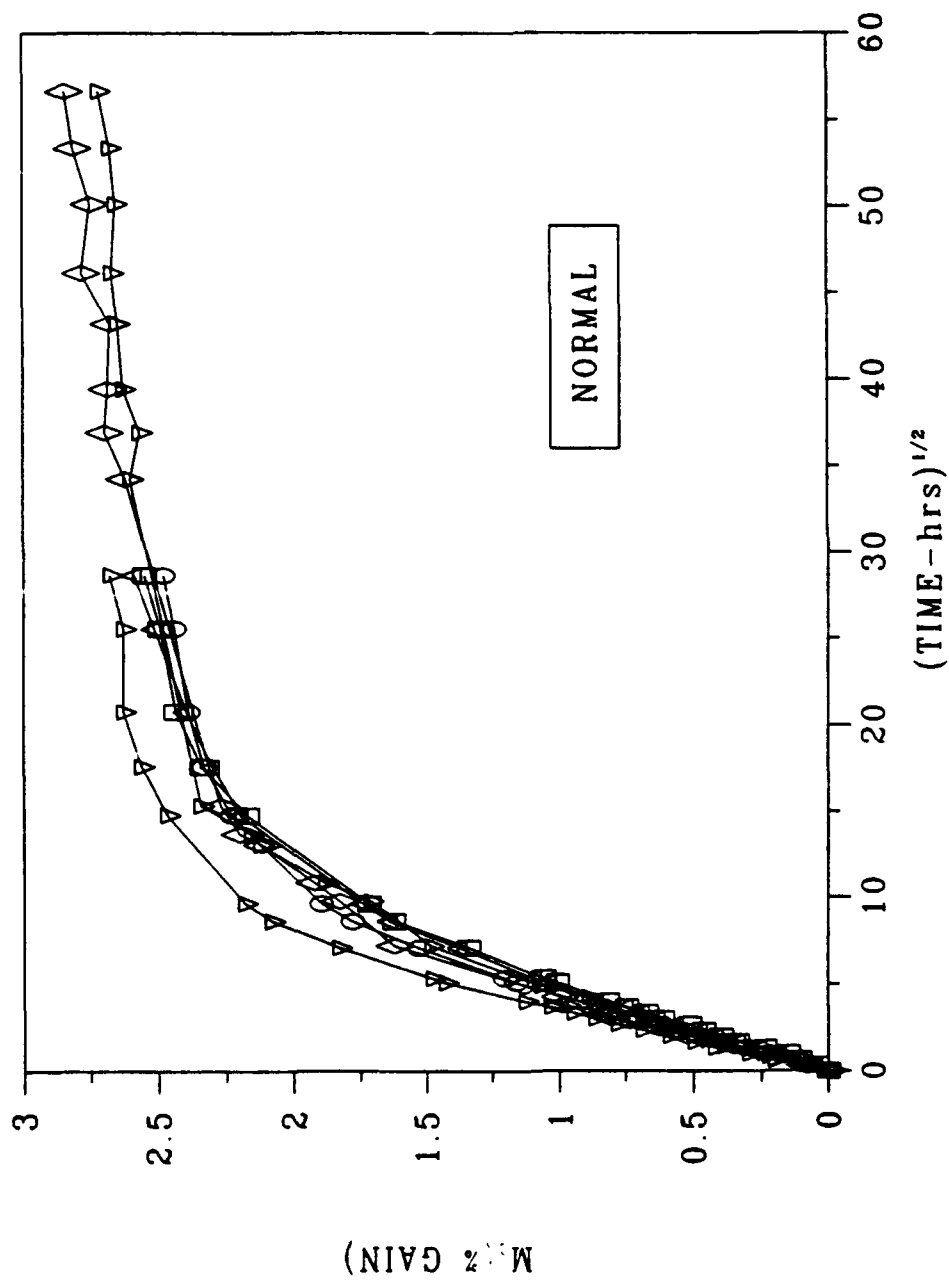


Figure 2. Diffusion curves for pure water absorption normal to the fibers in carbon/glass/vinyl ester composite. Temperature = 40°C.

ABSORPTION CURVES - 3% NaCl Soln

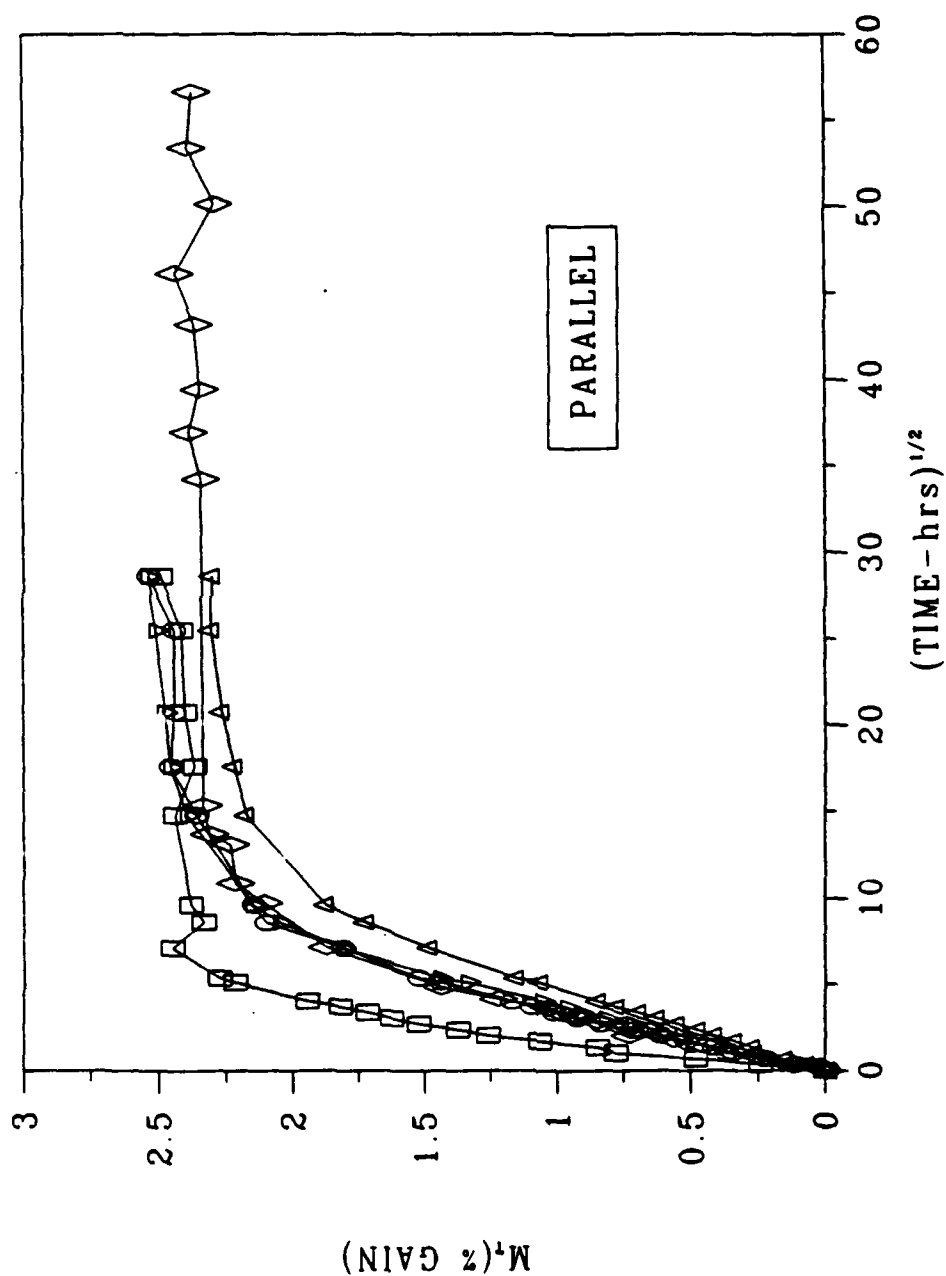


Figure 3. Diffusion curves for absorption of 3% NaCl solution parallel to the fibers in carbon/glass/vinyl ester composite. Temperature = 40°C.

ABSORPTION CURVES - 3% NaCl Soln

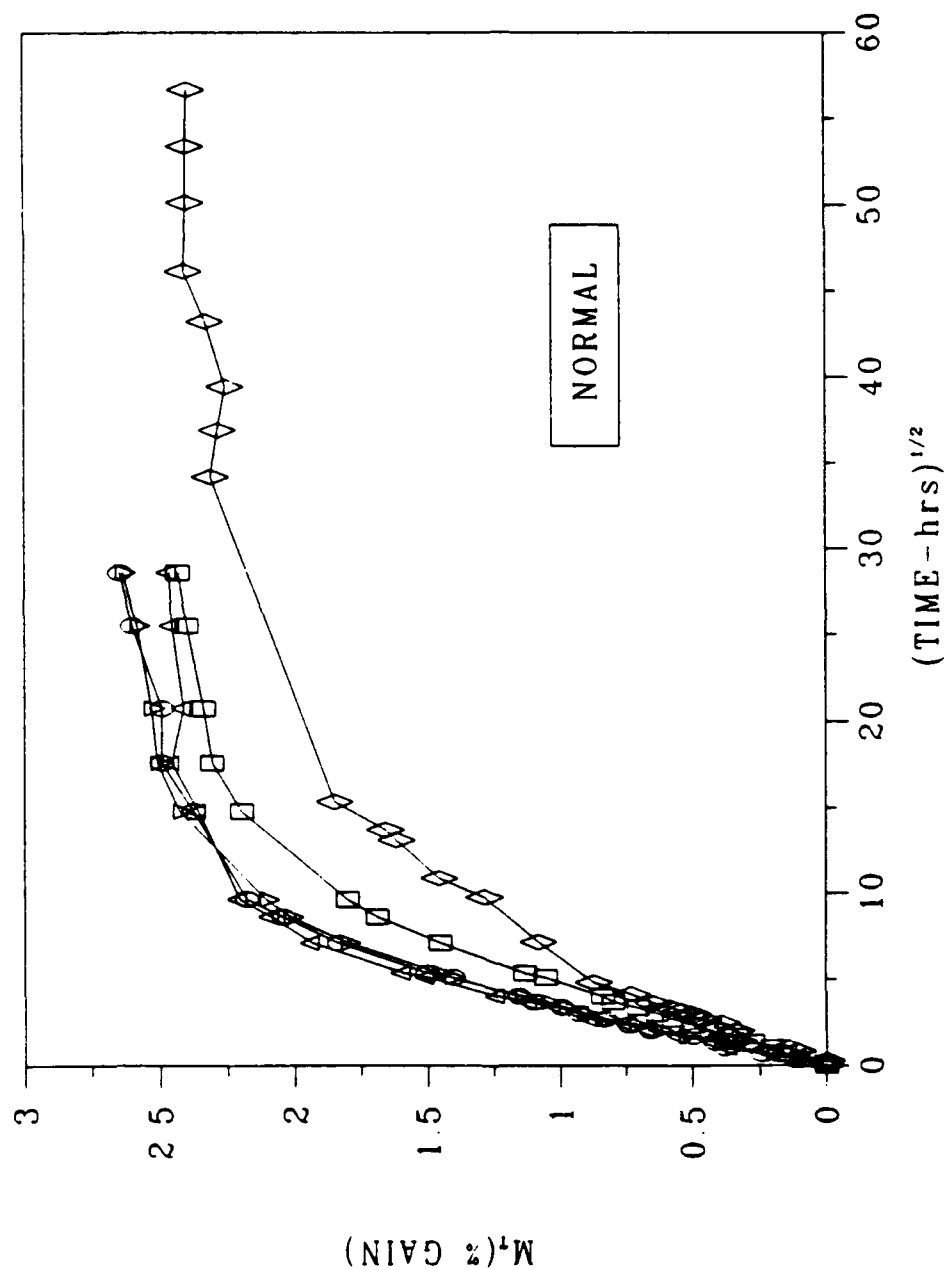


Figure 4. Diffusion curves for absorption of 3% NaCl solution normal to the fibers in carbon/glass/vinyl ester composite. Temperature = 40°C.

ABSORPTION CURVES - NEAT RESIN/PURE WATER

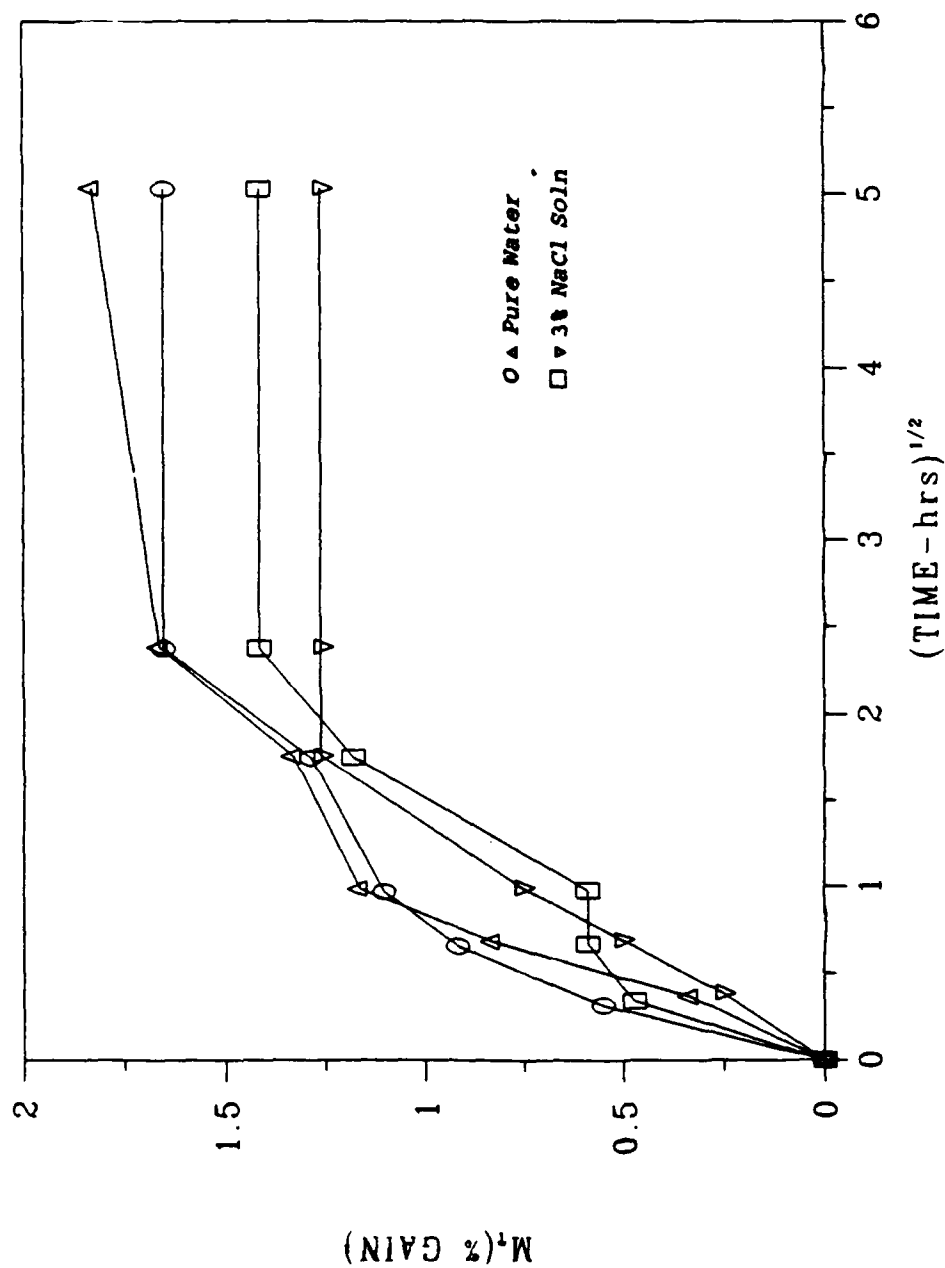


Figure 5. Diffusion curves for absorption of pure water and 3% NaCl solution in vinyl ester neat resin (as cast). Temperature = 40°C.

non-Fickian from these curves. Previous investigation by Lee [5] suggested a Fickian type absorption in similar vinyl esters. But the plateaus in the present curves support a two stage diffusion. However, this is unlikely for vinyl esters and the error could be attributed to experimental scatter. More data on water diffusion in neat resin is required to draw any conclusion. The saturation values for both the composite and the resin are presented in Table [1]. The water diffusion coefficients for the composite are also presented in Table [1]. It can be seen that the diffusion parallel to the fibers is higher than that normal to the fibers by an average 1.5 times. This is due to less obstruction in the direction parallel to the fibers. The D_p/D_n , however, is 15% lower for the case of 3% NaCl solution. Contrary to expectations, the average diffusion coefficients for pure water are lower than those for NaCl solution by 10% and 25% for parallel and normal diffusion respectively. These reductions, however, are within the range of experimental data scatter. The saturation values for the 3% NaCl are about 7% lower than those for pure water whereas theoretical prediction is that the reduction should be by about 3%. The explanation again is that these differences are within the range of data scatter. The average saturation value for the composite is about 2.5% whereas for neat resin it is about 1.6%. This huge increase of about 63% in water pick-up in the composite could be due to water accumulation at the interface because of debonding caused by water. Another possibility is the presence of thixotropes in the composite. Usually silica based thixotropes are widely used and these are greatly hydrophilic. In fact, trace amounts of silica found in the precipitates from blister fluids by EDAX analysis makes this look more plausible.

Table I

Average diffusional data from absorption experiments at 40°C

D_p = Diffusion coefficient parallel to fiber layers

D_N = Diffusion coefficient normal to fiber layers

M_{sat} = % wt gain at equilibrium saturation

CARBON/VINYL ESTER COMPOSITE				
Solvent	D_p $\times 10^8 \text{ cm}^2/\text{s}$	D_N $\times 10^8 \text{ cm}^2/\text{s}$	D_p/D_N	M_{sat} (wt %)
Pure water	1.56	0.91	1.82	2.6
3% NaCl Soln	1.72	1.20	1.53	2.4
NEAT RESIN - VINYL ESTER				
Pure water	-			1.75
3% NaCl Soln	-			1.40

GALVANIC BLISTERING :

Tucker and Brown [1] conducted tests to examine the effect of constant strain on the flexural strength of the carbon reinforced composite under seawater. This required the use of steel C-clamps fixed to the composite which resulted in the formation of a galvanic cell. The steel C-clamps severely corroded and the composite blistered. Subsequently, research was instigated to determine the cause of blisters.

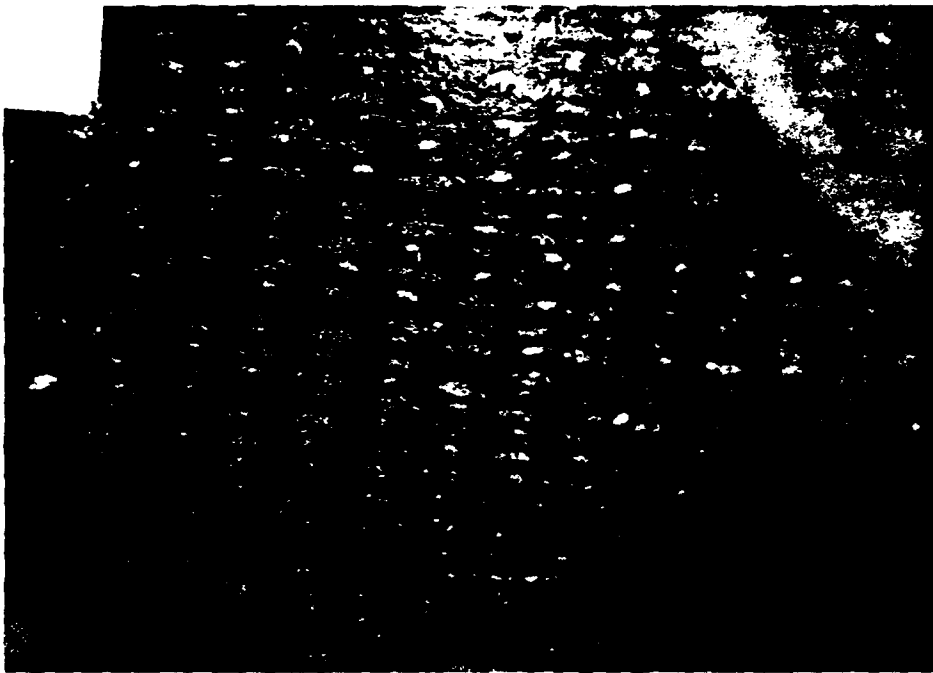
MORPHOLOGY OF BLISTERS IN CVE COMPOSITE:

Refer to the pictures shown in Figures [6a] and [6b]. Figure [6a] shows the blisters on the surface of the carbon/glass/vinyl ester composite. In this photograph (2X) the carbon tows run vertically whereas the glass tows run horizontally. The oval shaped blisters of size $1/8'' \times 1/16''$ can be seen at the locations where the fiberglass is exposed to view. They form a regular array. Although this gives an impression that the glass is somehow involved in the blister formation or that these locations could have been the only preferential sites; a careful examination reveals several tiny blisters away from the locations mentioned. For example, two such blisters are indicated by arrows in Figures [6a] and [6b]. In fact, numerous very small blisters form over the surface where the carbon fibers are closest to the surface. These have linear dimensions less than 0.5 mm and can be seen in photograph [6b]. Observations of blister formation are listed below:

(a) Very tiny blisters of a few hundred microns size form first where the carbon fibers are closest to the surface. This actually means the polymer film thickness is less here and quickly closes a galvanic cell. These blisters, as a result, seem to break open as soon as



(6a)



(6b)

Figures 6a, 6b. Photographs of galvanic blisters on carbon/glass/vinyl ester composite. (2X)

they form (within 24 hrs.). The white spots over the carbon fibers are these blisters (in Figure [6b]) (the white color of these blisters was due to the total internal reflection on the inner polymer surface created by delamination at the fiber/matrix interface).

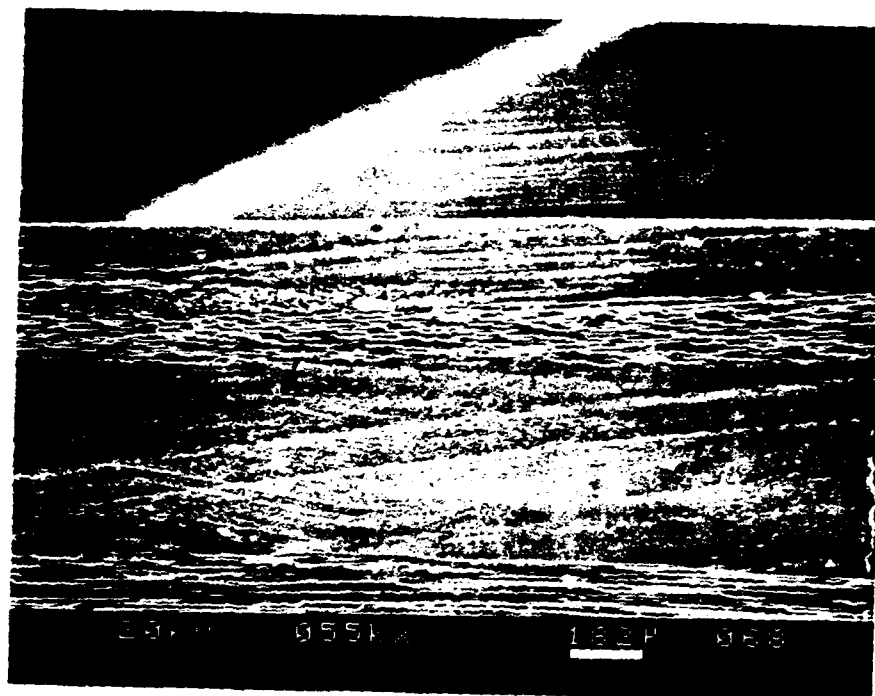
(b) After about 3 to 4 days, bigger blisters, initially of aspect ratio unity, form over the glass fibers. At first glance, it appears that the big blisters may be a result of glass degradation. However, the thickness (depth) of the polymer is at a maximum in this location and it is the thickness of the polymer film that results in bigger blisters. This is supported by the fact that blisters form at locations away from the glass fibers.

Also, subsequent experiments discussed in the next section eliminate glass as causative.

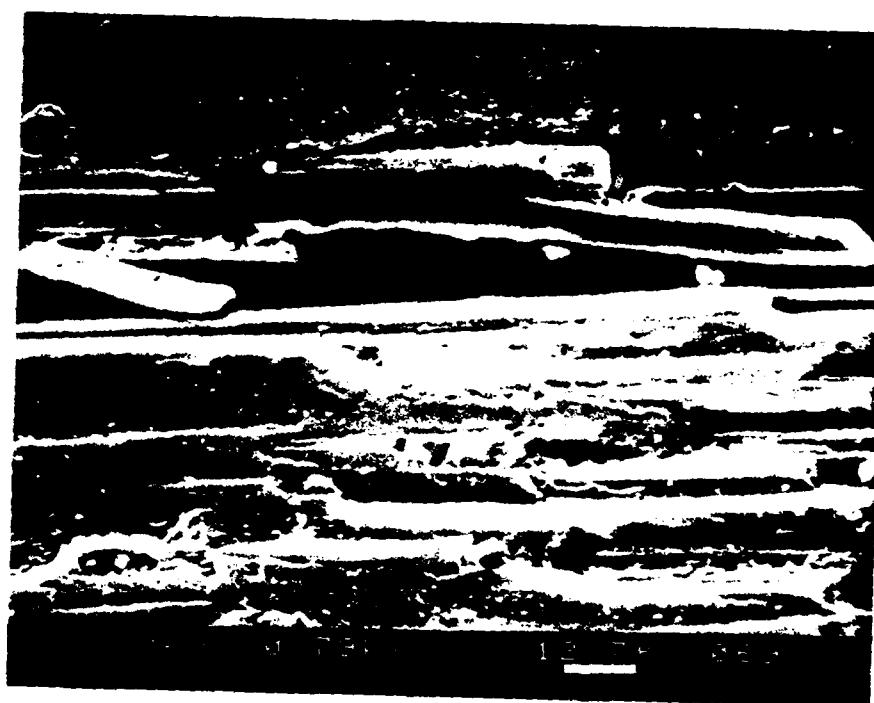
An SEM morphological study was conducted of the blisters. Figure [7a] shows a vertical section through a blister. The bright line running horizontally is the composite resin-rich surface. Below this line, a less brighter band (containing dashed lines) also running horizontally is the carbon fiber tow. Glass fibers can be seen as tiny dots (some of these glow due to charging) to the left side of the micrograph and just above the carbon fiber tow. To the right an opening along the carbon/matrix interface can be seen. This is the blister opening.

Figure [7b] shows this blister opening at a higher magnification. It clearly reveals that the blister opening occurred at fiber/matrix interface. However, a few fibers are seen attached to the blister cap. Actually, the blister opening occurs within the carbon fiber bundle but at the fiber/polymer interface.

Figure [7a] also shows that the interface crack proceeded below the glass fiber bundle. The fiberglass tows are unaffected by blisters. Figure [8a] supports this



(7a)



(7b)

Figures 7a, 7b. SEM micrographs showing delamination at the carbon/matrix interface in carbon/glass/vinyl ester composite.

observation. In the micrograph, to the left is shown the inside of a blister (i. e. the deformed polymer cap is removed and the interior was exposed for view). The oval shape of the blister can be seen in this view. The fibers that are running vertically are carbon fibers. At the top of this blister can be seen some fibers running horizontally. These are glass fibers. The region marked by the inset was magnified 10 times and is shown in the right half of the micrograph. Clearly, there is some polymer attached to the glass fibers and this polymer phase could be seen debonded from the carbon fibers. It indicates that the delamination is at carbon/matrix interface and also eliminates glass as contributory. However, it could be argued that the carbon fiber/matrix bond was weaker than the glass/matrix bond so that the delamination occurred at the carbon/matrix interface. But, in a virgin sample, it was observed that the glass fibers were more loosely bound to the matrix phase than the carbon fibers. This was checked by manually attempting to displace the fibers. Thus, it can be assumed that a degradation reaction is taking place at the carbon fiber/matrix interface which results in the debonding and delamination at the interface. Moreover, the galvanic conditions under which this is happening suggest that the interface reaction is of an electrochemical nature. Figure [8b] shows the magnified view of the carbon fibers in the delaminated zone. This picture shows carbon fibers that are totally clean and devoid of the polymer. This may mean that the polymer around these fibers was completely dissolved or it could be an artifact as a result of the blister cap been pulled open. If the former is true, the micrograph suggests that the polymer was involved in the degradation reaction. (This inference is drawn from morphology studies only).

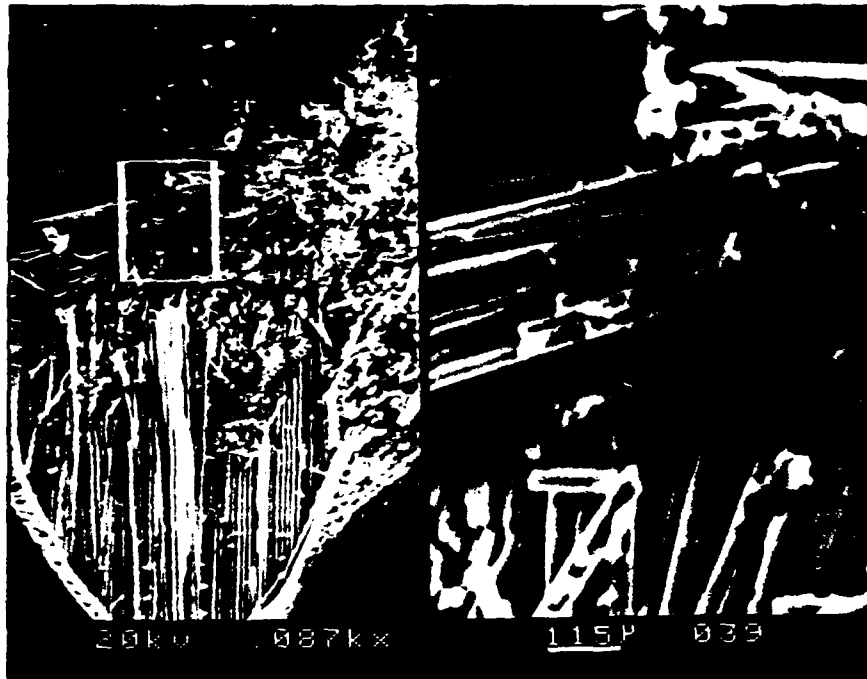


Figure 8a. SEM micrograph of top view of the interior of a blister in carbon/glass/vinyl ester composite.

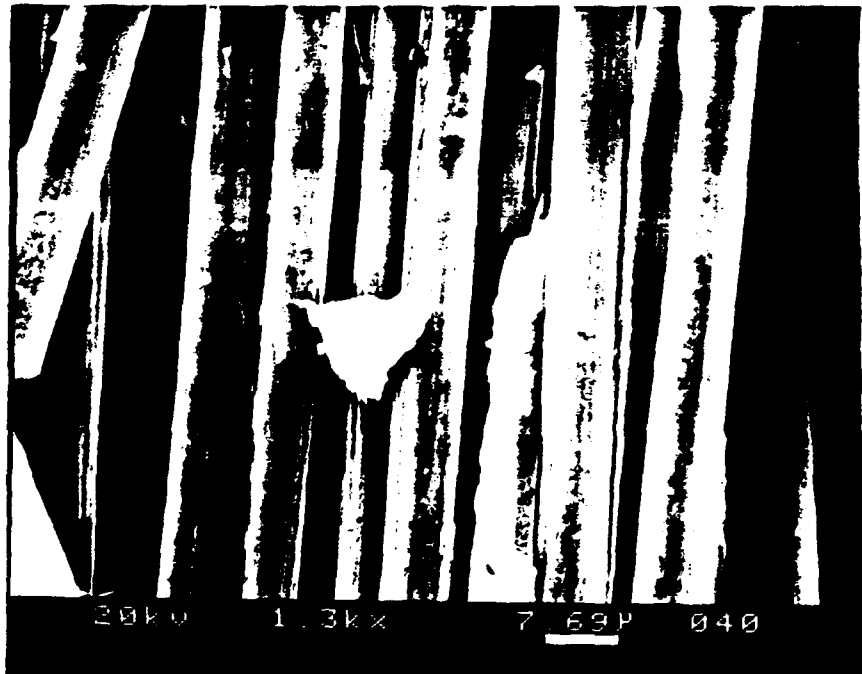


Figure 8b. SEM micrograph showing magnified view of the carbon fibers seen in the blister of Figure 8a.

CAUSES OF GALVANIC BLISTERING:

Initially it was thought that the fiberglass present in the reinforcement was attacked by the water. But samples which are galvanically isolated even after eleven months of immersion did not show any sign of blistering. It was thought that the high pH environment over the cathode (due to oxygen reduction) might have attacked the glass fibers. A series of experiments were performed to eliminate several variables and to draw the basic conditions required for the galvanic damage of these composites. The experiments and the observations were discussed below:

- (1) A composite, made of T300 carbon fibers with fiberglass wefts in DERA KANE vinyl ester, galvanically coupled to steel in seawater blistered.
- (2) Same composite also blistered in 3% (by wt) NaCl solution. This says that a simple electrolyte is sufficient to create conditions for galvanic blistering. All subsequent experiments were performed with 3% NaCl solution.
- (3) A composite, made up of T300 carbon fibers plain weave (no fiberglass) and DERA KANE vinyl ester, under galvanic coupling conditions blistered in 3% NaCl solution. This leads to a conclusion that the glass is not an essential element for the galvanic blistering.
- (4) Disks were cut from a solid graphite cylinder, dipped in vinyl ester resin and allowed to cure at room temperature. These special samples were designed primarily to form large blisters so as to produce adequate amounts of blister fluids for their chemical analysis. These flat plate graphite reinforced composite also blistered under galvanic coupling with steel. This experiment eliminates the role of several variables such as

coupling agents, sizing agents, binders used for fiber treatment, as causes for this type of blistering. However, it should be noted that the graphite material used is hot pressed and contains a tar binder.

It appears that the fundamental requirements for galvanic degradation of polymer composites. They are:

- (1) a cathodic surface (carbon fibers)
- (2) a polymer film attached to this surface which becomes a solid electrolyte during solvent electrolyte absorption.
- (3) a galvanic couple with this cathode and
- (4) an electrolyte solution such as sea water.

The problem has taken a more general form. The question that arises now is whether the polymer is involved in the blistering process or is it merely a transport medium? Since the cathode cannot be attacked and all other variables have been eliminated, the blister producing products must form either as a result of cathodic reaction or a product of cathodic reaction must in turn break down the polymer. However it is difficult to observe polymer degradation (if any) in a carbon composite due to the black carbon background. Therefore, a thin film of vinyl ester was cast on a platinum foil. This was galvanically coupled to steel in 3% NaCl. Although blisters formed, most of the polymer surface did not deform at all. This is because the metal/polymer interface was so weak that as soon as delamination occurs at one point it spreads rapidly in all directions, thus debonding the whole polymer film from the metal surface. In fact, the polymer film peeled off easily when pulled by hand.

A significant observation was made by way of this experiment. Figure [9a] shows the Pt foil with the polymer film, taken after 2 day of galvanic coupling. The white patches did not exist before coupling formed on the Pt surface. These patches were of irregular shape and randomly formed. It was thought these patches could be some type of deposits or degraded regions of polymer. To check this, a rectangular piece of the film was cut out as shown in the Figure [9a]. As soon as the cut reached the edge of the patch, the unaffected region of polymer just popped up. Moreover, scratching the white patch region produced white powdery substance. No polymer film was found below this patch. The indication is that the polymer in this region was destroyed. When the whole polymer film was peeled off the Pt surface, these patches were left on the Pt. The film carried over the holes in those places. The film was observed under Transmission Light Microscope. Refer to the photomicrograph (10X) in Figures [9b] and [9c]. Figure [9b] shows the circular region where the polymer was lost. In addition, the rough surface around this hole indicates that the polymer in this region was also subjected to degradation. Figure [9c] is a magnified view (40X) of the inside edge of the hole formed in the polymer film. The degradation of the polymer in this picture is evident.

Thus, we have an indication that the polymer is degraded either due to its direct involvement in a cathodic reaction or due to chemical attack by a product of cathodic reaction. In addition, this degradation is not taking place uniformly all over.

The basic questions remaining are:

- (a) What is the reaction that is responsible for the polymer degradation?
- (b) What are the preferential sites for the degradation or blister formation.



Figure 9a. Photograph showing white patches formed in the polymer film on Pt surface after galvanic coupling for 24 hours. (10X)



Figure 9b. Photograph of Polymer film peeled off the Pt surface. A hole stands in the place where the polymer disappeared. (10X)

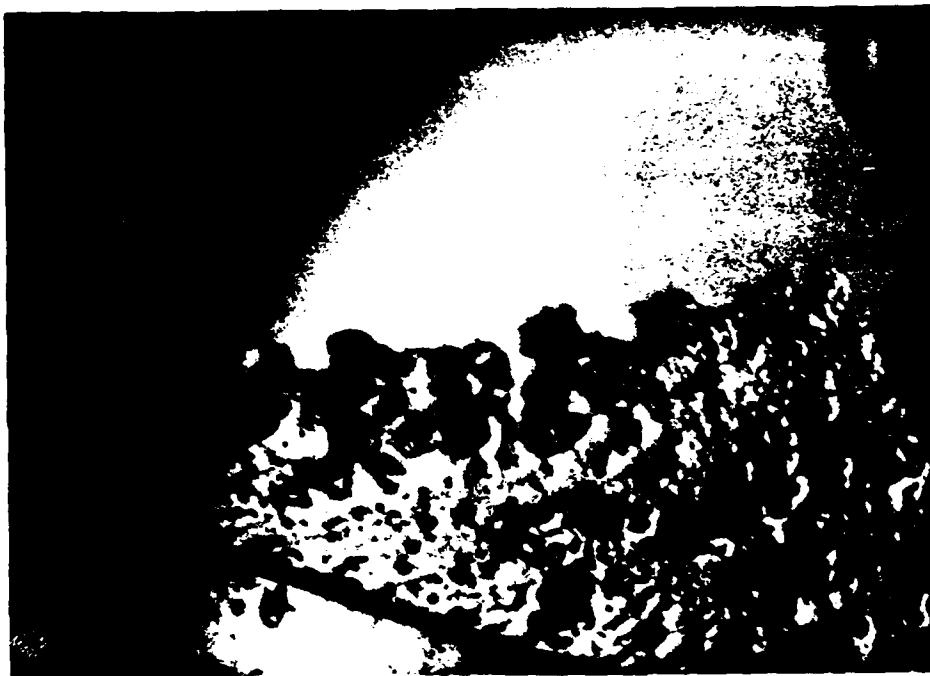
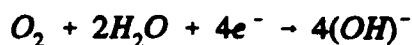


Figure 9c. Photograph revealing Polymer degradation on Pt surface.
(40X)

The most widely occurring cathodic reaction is



It was thought that the hydroxyl ions produced by oxygen reduction according to above reaction would have been attacking the polymer. However, a two week exposure test of vinyl ester samples in 0.1, 1.0 and 10 N NaOH solutions did not result polymer degradation. Thus, the possibility of direct attack on the polymer by hydroxyl ions was eliminated. The question remains; what is causing the polymer to degrade? Sloan *et al* [3] stated that an intermediate stage in the production of hydroxyl ions by oxygen reduction is the generation of perhydroxyl ions (HO_2^-). These perhydroxyl ions are several hundred times more reactive than hydroxyl ions. They suggested that these perhydroxyl ions may be reacting with the electrophilic centers in the polymer chain such as the ester bonds resulting in polymer degradation. Before proposing any other mechanism the analysis of blister fluid is undertaken. The knowledge of the products in the blister fluid and the polymer used to begin with together should provide further information.

SAMPLING OF BLISTER FLUIDS:

The task of collecting blister fluids was found to be a formidable one. An average sized blister on the fibrous composite yielded fluid less than 1 microliter. The maximum size of the blisters in these composites is dictated by the widths of the fiber tows. As the blister growing on a tow reaches the adjacent tow, its growth is hampered by the reinforcing effect of the neighboring tows. Therefore, the fluid yields are small. Even the use of glass micropipettes of size 0.004" ID proved to be fairly effective in the

collection of these tiny quantities. Therefore to obtain larger quantities of blister fluids, we need bigger blisters. Since, as discussed above, one cannot get bigger blisters on the fibrous composite, an effective method was devised. A vinyl ester composite was made with solid graphite disc as reinforcement. Several of these were galvanically coupled with steel in 3% NaCl solution. Since there is no obstruction whatsoever for blister growth, bigger blisters resulted with sizes as big as 4mm dia. Sufficient amounts of fluids were collected using micropipettes of sizes .25 and .5 microliters. The analysis of blister fluids is underway.

Fourier transform infrared spectroscopy (FTIR) is a technique used to identify the molecular structure of organic compounds. Since the blister fluid might contain more than one degradation products, information from high performance liquid chromatography (HPLC) experiments which gives number of compounds and from mass spectroscopic analysis which gives molecular weights is necessary in conjunction with the FTIR results in order to identify the compounds in the blister fluid.

FTIR Analysis: As a first step of the process, the FTIR spectrum of the blister fluid is obtained. This spectrum is shown in Figure [10a]. The wide peak between 3000 and 4000 cm^{-1} and the band between 1500 and 2000 cm^{-1} are identified to be that of water. However, a small peak where the vertical cursor stands is characteristic of the blister fluid. The blister fluid being alkaline in nature, the presence of alcohols in the blister fluid may be suspected. FTIR spectra of methanol and ethanol were obtained. The peak referred to in Figure [10a] is spread out and is compared with the methanol and ethanol spectra in Figures [10b] and [10c] respectively. The particular wave number range

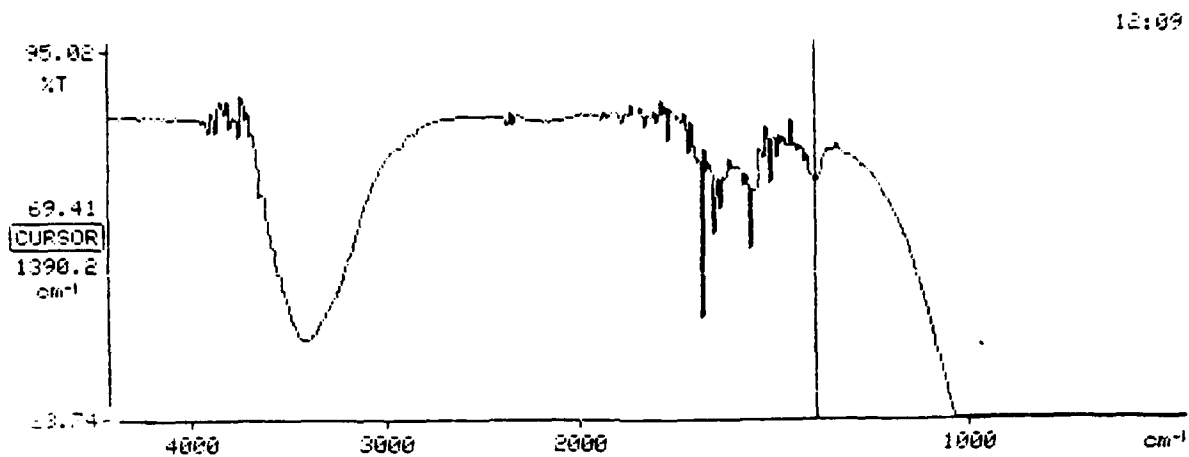


Figure 10a. FTIR spectrum of blister fluid

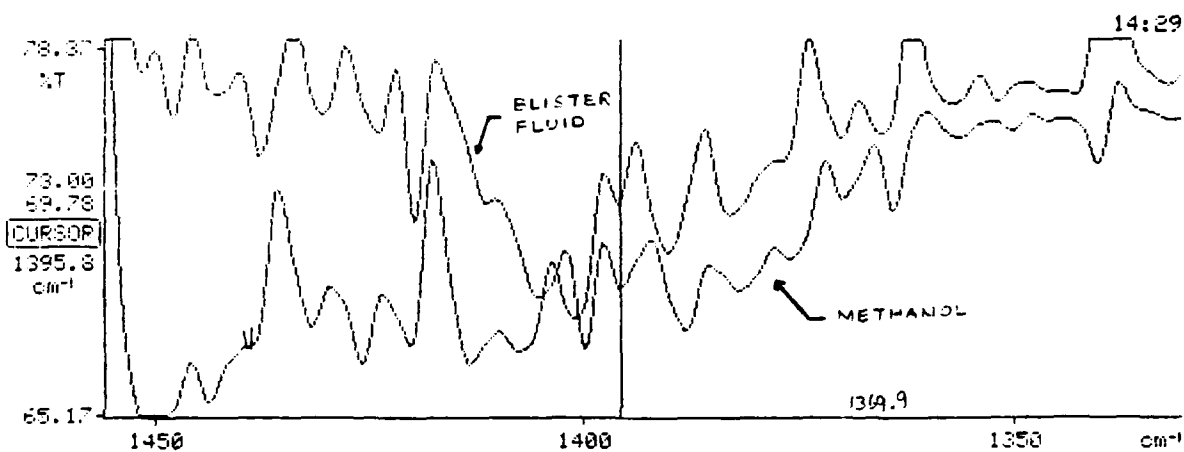


Figure 10b. Comparison of FTIR spectra of blister fluid and methanol.

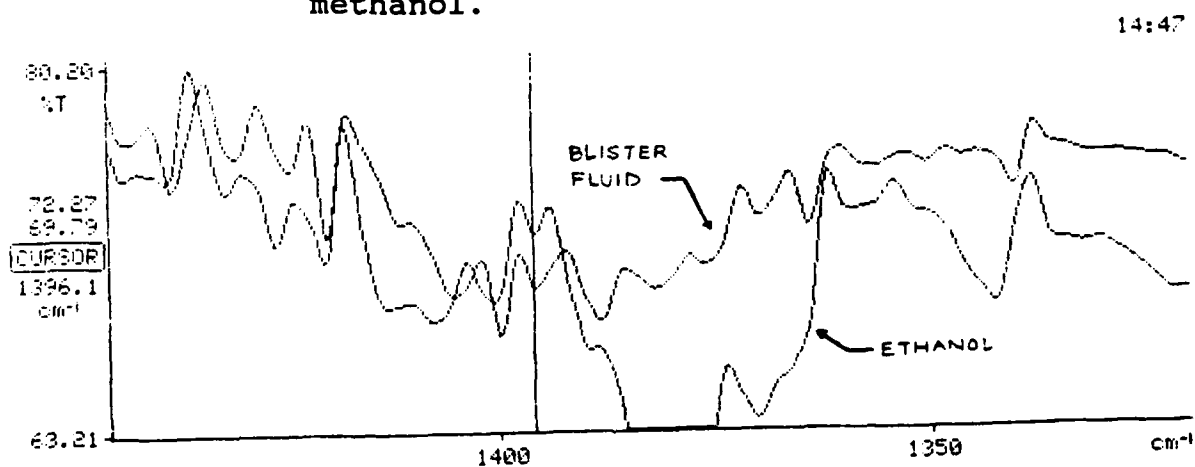


Figure 10c. Comparison of FTIR spectra of blister fluid and ethanol.

showed is typical of O-H stretching vibrations of alcohols. These spectra reveal that the blister fluid spectrum closely follows those of methanol and ethanol although differs considerably in intensities and by minor shifts. This suggests the presence of alcohols or glycols. However what kind of alcohols is unknown. The following FTIR spectra are being obtained:

- (a) blister fluid,
- (b) unpolymerized vinyl ester,
- (c) degraded polymer on Pt cathode surface,
- (d) polymerized vinyl ester,
- (e) water soluble compounds of vinyl ester resin.

Analysis based upon the above spectra should allow us to guess the probable compounds of the blister fluid. Then standards of those compounds will be run to check their presence. Since the blister fluid is aqueous based, strong peaks due to water might mask out the peaks of blister fluid elements. Therefore, efforts will be made to dissolve the blister fluid components in a suitable solvent to produce a better spectrum.

GCMS Analysis: Recently analysis of blister fluid by gas chromatograph coupled to a mass spectrometer has been performed. The solvent used was methylene chloride/acetone solution (200 microgram/liter) and the carrier gas used was helium. A 5% phenyl based capillary column was used. The chromatogram obtained is shown in Figure 10(d). The spectrum does not show any significant peaks. The reason could be that the blister fluid precipitates may not be soluble in the solvents employed or the material may not be eluting from the column. Further efforts to analyze by mass spectrometry will be made

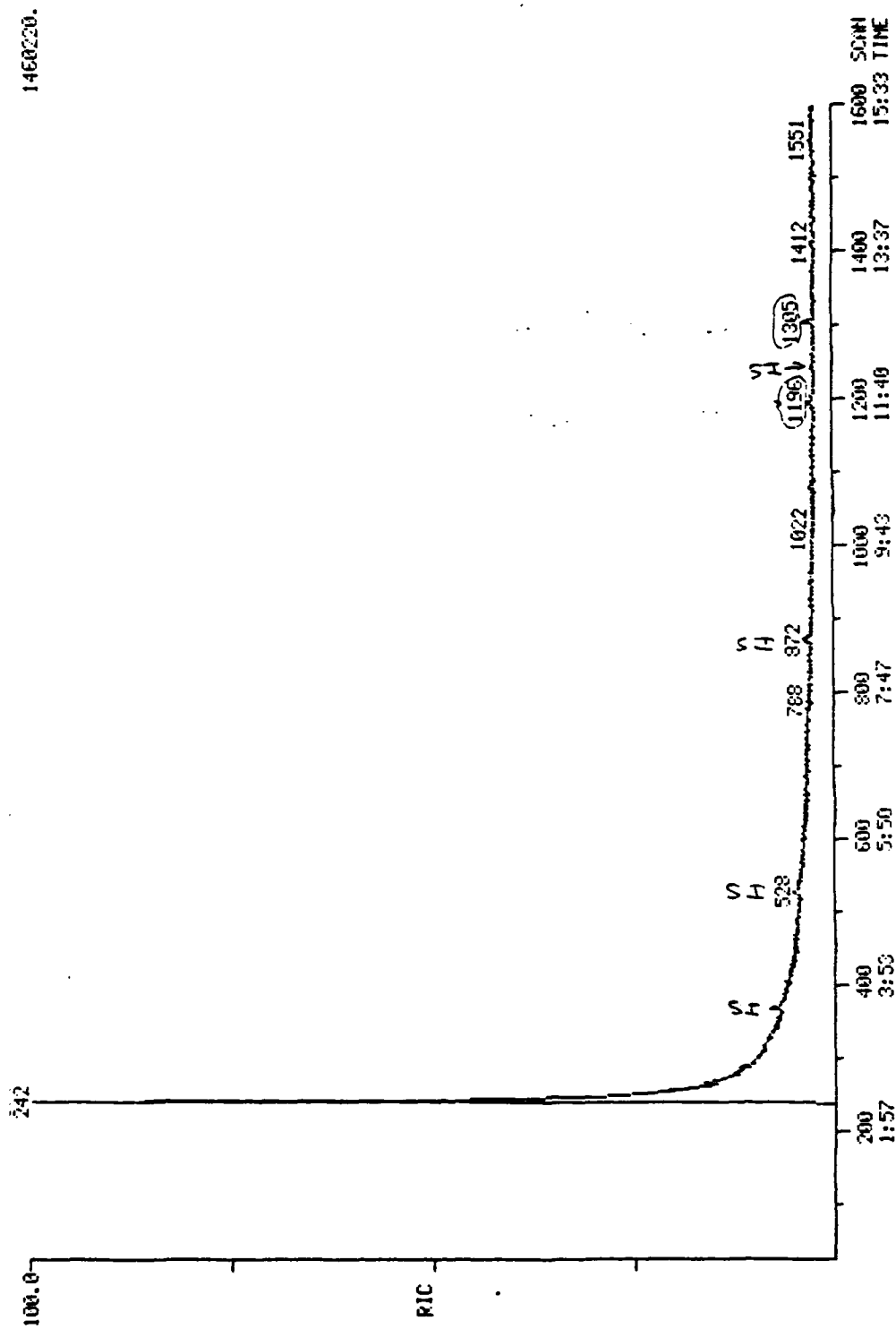


Figure 10d. GCMS spectrum of blister fluid.
IS = internal standards.

after analysis by HPLC.

HPLC Analysis: A gel permeation chromatographic column which is compatible with aqueous solutions has been obtained for use on the Waters model 4000 HPLC for sample separation. This method is widely used for analysis of polymer extracts.

Experiments are underway to develop the time constants for a series of standards.

SEM EDAX Analysis: Energy dispersive analysis was performed on the precipitates from the blister fluid. The spectrum is shown in Figure [11]. The spectrum indicates an Au, Si, Ag, Cu and Zn peaks. The Au peak is due to the sputtered gold coating, Ag from the silver paint used, and Cu and Zn were picked up from brass specimen holder. Therefore there is no evidence of low molecular weight species in considerable amounts in these crystals except for trace amounts of sodium, chlorine and silica. The pictures of the precipitates is shown in Figure [12a], [12b] and [12c]. Figure [12a] reveals needle shaped crystals in the residue. Even at a higher magnification (3700X) the crystals are seem to be needle or spindle shaped. The photomicrograph also reveals that besides these crystals there is some non-crystalline material or material which does not have these needle type shapes.

Many of these findings were summarized and presented at the First International Symposium on Advanced Materials (sponsored by the National Association of Corrosion Engineers) which was held in San Diego during June, 1991.

BLISTER FLUID ANALYSIS - EDAX-2

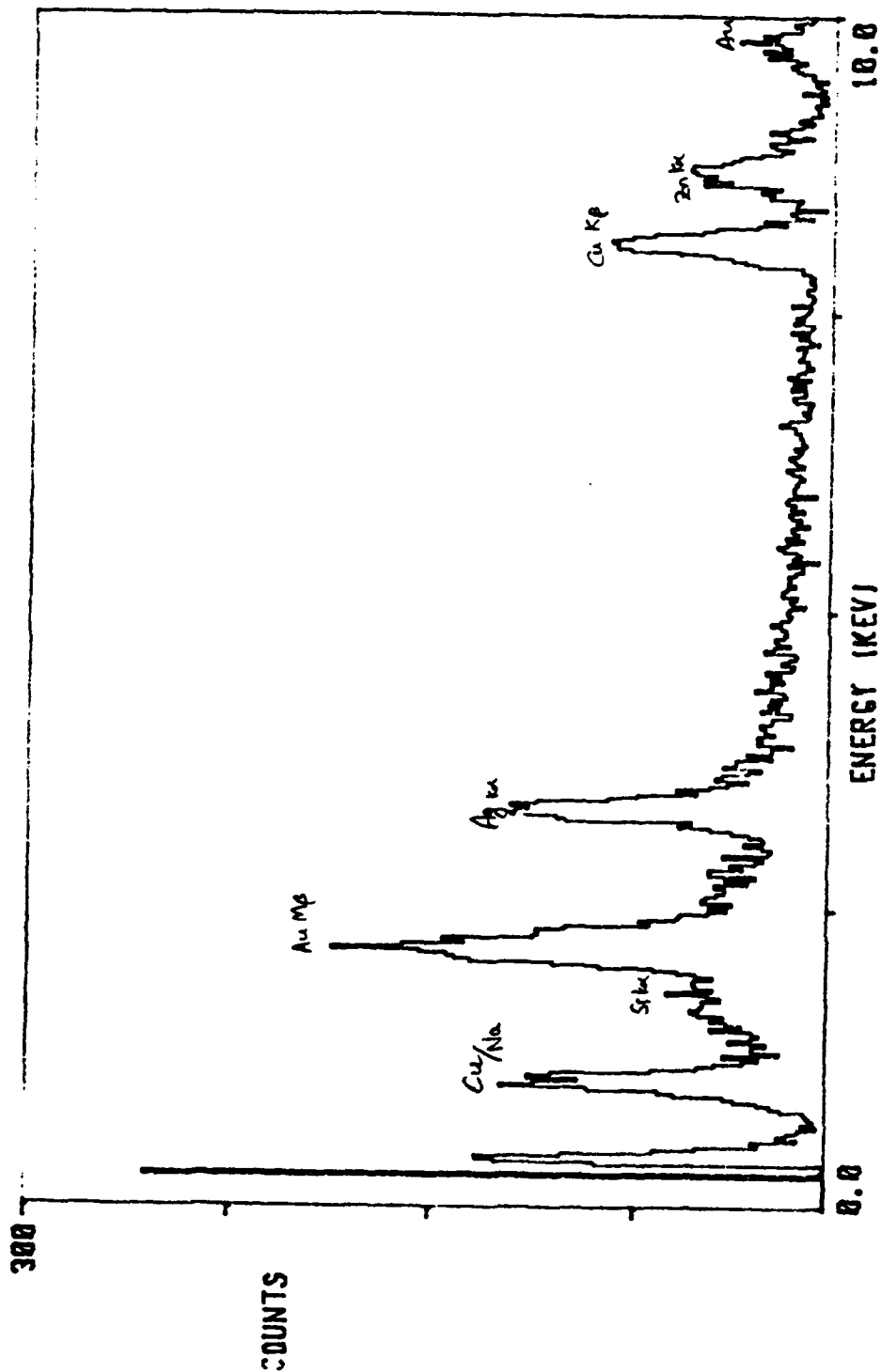


Figure 11. SEM EDAX analysis spectrum for blister fluid precipitates.

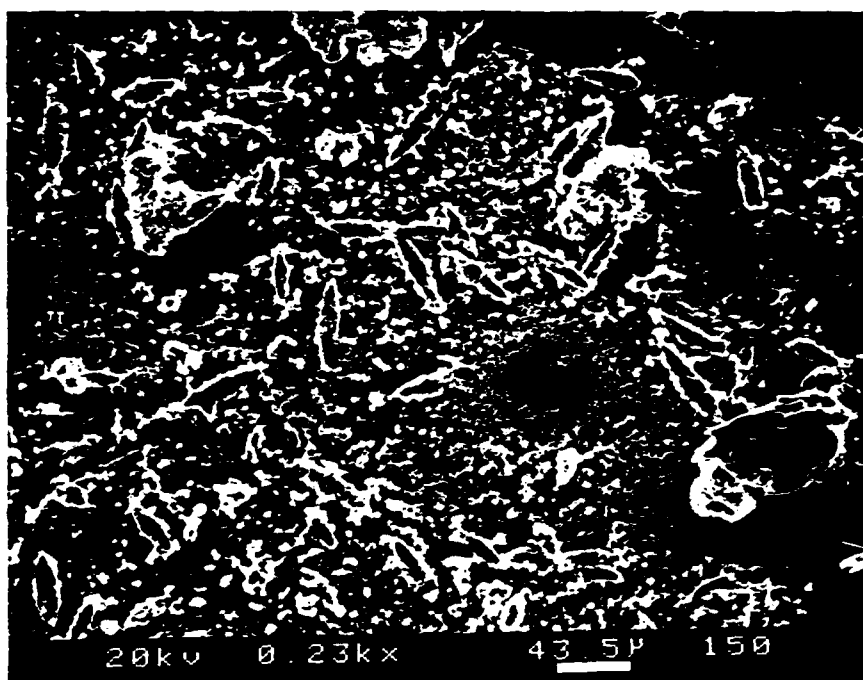


Figure 12a. SEM micrograph showing spindle shaped precipitate crystals of blister fluid.

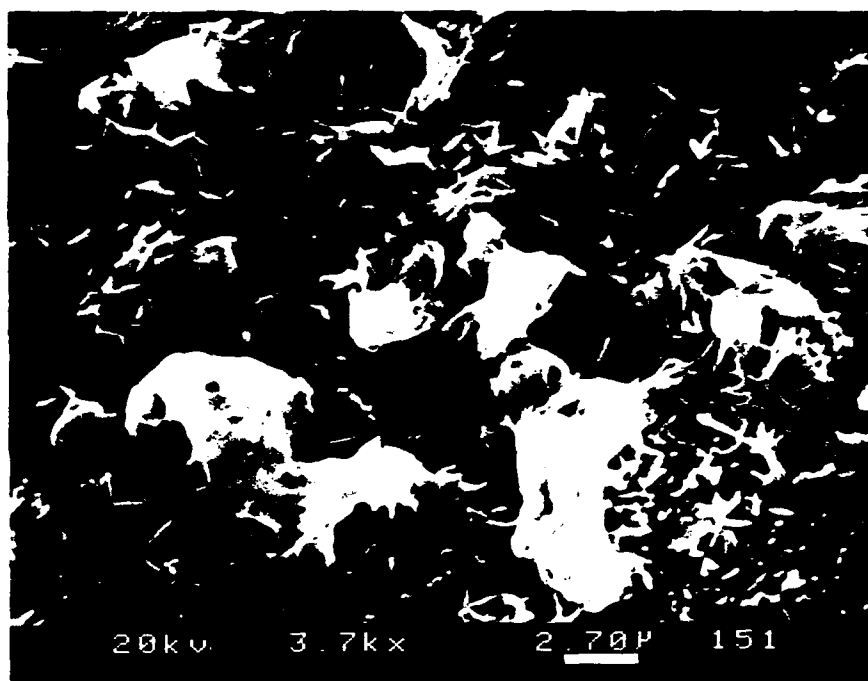


Figure 12b. SEM micrograph showing blister precipitate crystals at higher magnification.

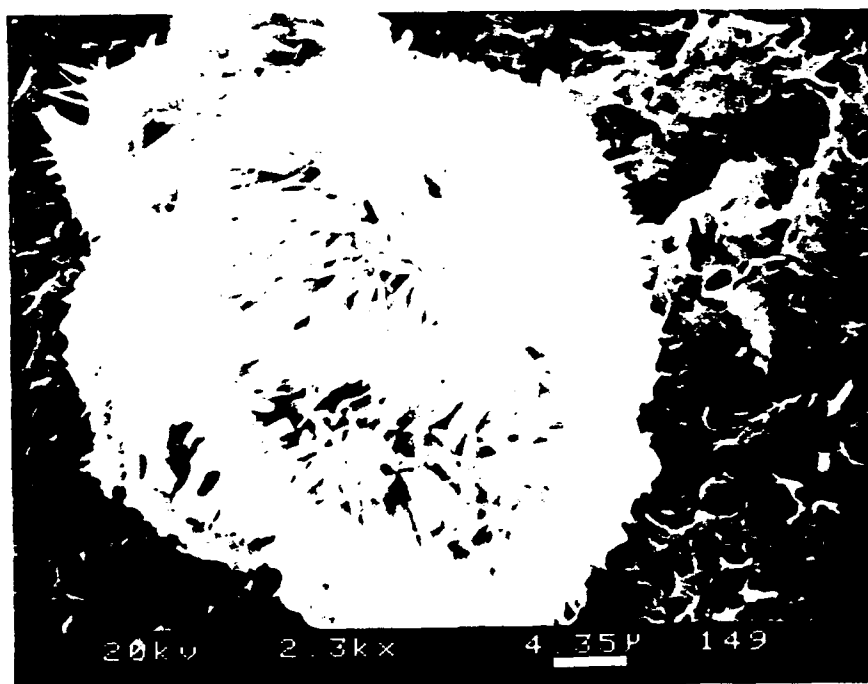


Figure 12c. SEM micrograph showing blister ppt crystals growing in all directions from a single nucleation site.

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