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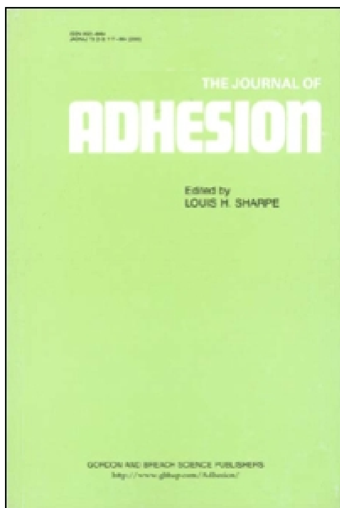

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Blistering of Glass-Epoxy Amine Adhesive Joints in Water Vapour at High Pressure. An Indication of Interfacial Crumpling*

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When joints are made between solids, the surfaces of which are soluble in water, with an epoxy-amine adhesive, blistering is observed in water vapour at high temperature and pressure. The occurrence of these blisters follows the cavitation theory in elastomers. Microscopic observation of the blisters suggest that they come from initial smaller ones which are homogeneously spread along the interface (not air bubbles or defects) and grow under the osmotic pressure developed by water condensation in the initial "sucker" and by surface dissolution. These observations led us to suggest that the solid/adhesive interface crumples during hardening of the adhesive and that many small suckers exist along the interface. This leads to a new model for the loss of adherence of epoxy-metal joints kept in high humidities.

KEY WORDS adhesive; epoxy; glass; joints; durability; interface; interphase; blisters; capillary condensation.

1. INTRODUCTION

As adhesive users, we are concerned with the loss of adherence of epoxy-amine bonded joints in humid environments. Thermodynamic evaluation[1] indicates that these joints cannot be stable when exposed to water and the loss of adherence has been attributed to the weakening of ionic bonds between the substrate and the adhesive.[2] Such bonds have been identified in some cases.[3,4] However, we have observed that, under normal conditions, there exists a threshold at 70% RH where the detrimental effect of water appears.[5]

In this work, we try to explain the origin of the humidity threshold and give some evidence that it could be due to microscopic voids that form along the interface during the curing process.

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2. LOSS OF ADHERENCE OF ADHESIVE JOINTS DUE TO WATER

In this section, we recall the main experimental results concerning the successive steps which occur during exposure of adhesive joints to a humid environment.

2.1 The Threshold of Humidity

When a joint is cleaved by a wedge, the adhesive is cracked over a length l_0. This crack seems indefinitely stable in indoor conditions, where humidity levels vary between 40 and 60%. When placed in an atmosphere of increasing relative humidity, the crack in this joint will increase in length when the relative humidity exceeds 70%.[5] The locus of fracture moves from inside the adhesive to the interface.

This observation that we first made on stainless steel/epoxy-amine adhesive joints has been confirmed by Lefebvre *et al.*[6] on glass/epoxy-amine interfaces and we noticed that it existed also with the various epoxy-amine adhesives that we use (Fig. 1).

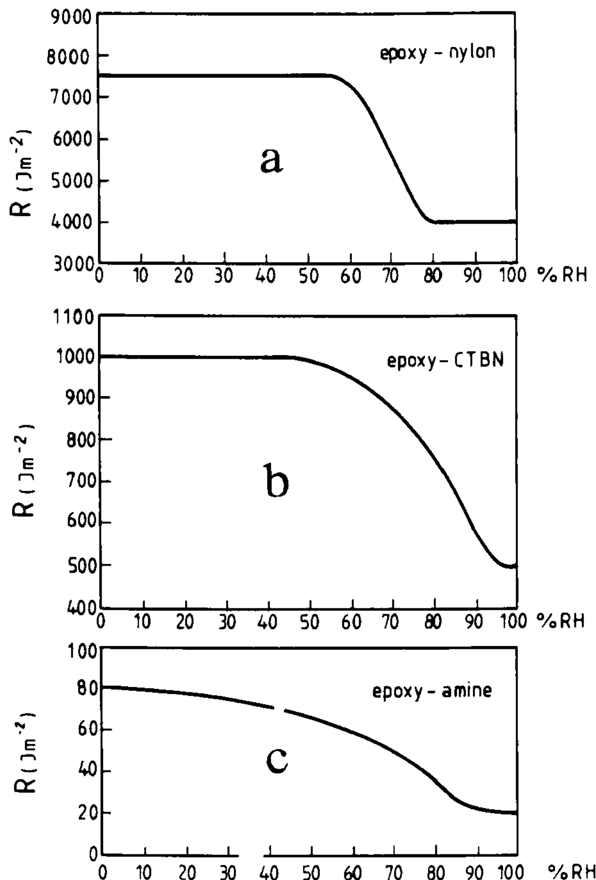

FIGURE 1 (Epoxy-amine)-stainless steel joints lose their resistance to fracture above 70% RH: a) 1-component, modified epoxy-nylon-amine; b) 1-component, modified epoxy-amine; c) 2-component, liquid epoxy-amine.

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2.2 Diffusion of Water

It is known that the weakening of adhesive bonds exposed to high humidities follows the ingress of water by diffusion into the polymer.[2] As water penetrates, it first binds to polar sites[7,8] and at higher concentration forms clusters.[8,9]

As shown by Arrowhime *et al.*,[10] the concentration of water in an epoxy-amine adhesive depends upon the surrounding humidity level. Thus, a threshold in ambient humidity corresponds to a critical concentration of water in the adhesive. Actually, Kinloch *et al.*[11] established that adhesive bond weakening occurs above a critical concentration of water in the adhesive. However, the reason that such a threshold exists is puzzling. Because the chemical potential of water is a logarithmic function of the relative humidity, one would expect a continuous degradation of the bond rather than a threshold value. A threshold may be expected, however, if capillary condensation occurs as we explain in the next paragraph.

3. Capillary Condensation in Pores

When water vapour adsorbs in porous solids, the pores of which have diameter ϕ, it will condense when its chemical potential is equal to that of the liquid. The partial pressure, P, at which condensation occurs is related to the saturating pressure, P_o, the surface tension, γ ($=72$ m Jm^{-2}), and the molar volume, V ($=18\times10^{-6}$ M^3), of water through the Kelvin equation (1). As the relative humidity is P/P_o one may write

$$RT \ln P/P_o = \gamma V/\phi \tag{1}$$

When $P/P_o = 0.7$, condensation occurs in pores of diameter 65 Å. If such pores were to exist along the interface, their filling by water would explain the weakening of the substrate adhesive bonding.

Interfacial condensation has been demonstrated by Nguyen *et al.*[12] at the germanium/epoxy interface and Koutsky[13] has described the formation of small nodules (75–250Å) along the solid/epoxy-amine adhesive interface. Our attempts to see this porous structure with a microscope were unsuccessful, so we tried to prove their existence by making them larger.

4. EXPERIMENTAL

4.1 Preparation of Joints

Joints were formed with epoxy resin Shell 828 EL, cured with Jeffamine D230 (Texaco), between a small disc of tempered glass (diameter 12 mm, thickness 0.15 mm) and various substrates, in the form of a rectangular plate (Fig. 2).

Various adhesive thicknesses were obtained by placing a drop of adhesive of various volume under the center of the disc. The drop spread evenly by capillarity giving joints of thickness 5 to 50 μm (measured with a comparator from the lower plate and subtracting the upper plate thickness with precision ± 2 μm). The adherends were cleaned in a basic solution, thoroughly rinsed with tap water, D.I. water and isopropyl alcohol, then dried with hot air. The adhesive was cured 4 hours

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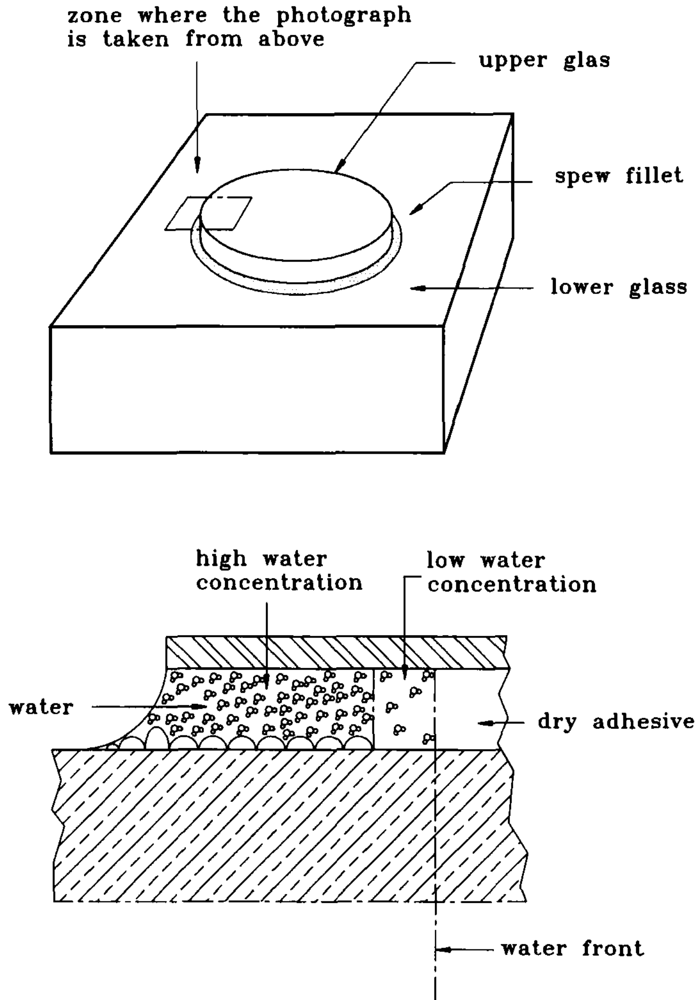

FIGURE 2 Schematic description of the glass joints used (above) (with indications of the conditions in which photograph of Fig. 3 was taken) and cross section explaining what is seen on Fig. 3 (below).

at 60°C and annealed for 1 hour at 120°C giving a polymer with a glass transition temperature (T_g) of 80°C (by DSC).

The various substrates were:

—soda lime glass (microscope slide)
—copper
—stainless steel
—sapphire

4.2 Bubble Formation

Joints made of glass were placed in a pressure cooker at 120°C, 1.2 atmospheres, and removed from time to time for observation. As water enters into the adhesive a region full of bubbles develops in a circle along the front of water (Fig. 3). These

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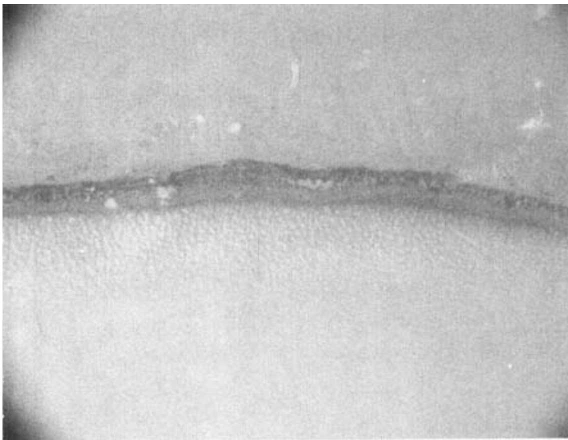

FIGURE 3 As water enters the adhesive joint, above T_g, a band filled with bubbles develops. On the photograph they are seen between the spew fillet and a clear zone where some water is present but bubbles have not yet formed.

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bubbles are not defects which are often present, here and there, in adhesive joints. Their distribution is homogeneous. They are not small bubbles that grow, either; when they appear, they all have the same diameter. That size seems to be related to the adhesive thickness ($\phi \sim e$) as long as the thickness is lower than 16 μm. For thicker joints the diameter of the bubbles remains at 16 μm. It is only when the first bubbles have appeared that they will increase in size upon further exposure to the pressurized water vapour and finally merge into channels. The bubbles only appear along the rectangular lower microscope slide and not along the upper one.

4.3 SEM Observation of the Bubbles

In order to observe the shape and the localization of the bubbles, we scribed both glasses and broke the joint. In so doing we formed, by chance, a spike on the upper glass from which the lower glass delaminated interfacially, leaving the blistered adhesive surface free (Fig. 4).

The part of the joint bearing the spike was placed in a SEM after metallization with a thin film of gold (*ca.* 1000Å). Upon viewing the sample inclined at 45° the bubbles appear as blisters *ca.* 0.6 μm deep with a small dark point at their top (Fig. 5).

5. CAVITATION AND BLISTERING

There are cases in which blisters appear suddenly with a macroscopic size along the interface; their formation occurs only in boiling water or in the pressure cooker. This can be explained by the theory of cavitation in rubbers. At these temperatures, above T_g, the adhesive is rubbery and has a low elastic modulus, $E = 20$ MPa (Fig. 6). When joints are left for one year in water at room temperature no bubbles are observed.

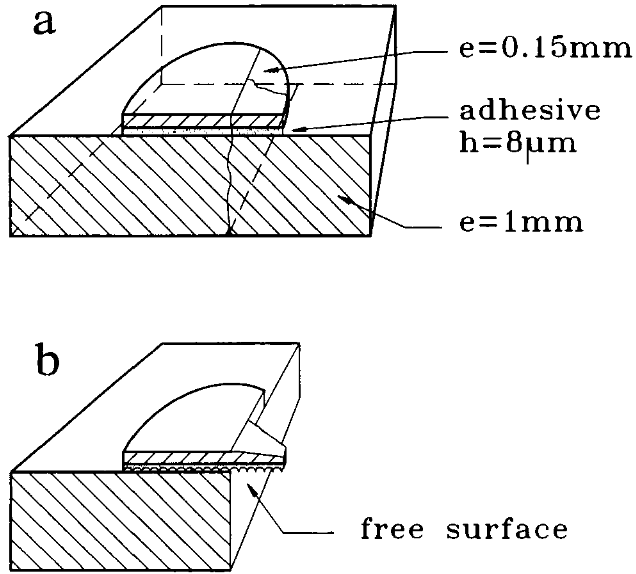

FIGURE 4 a) Dimensions of the glass plate. b) Upon breaking, a "spike" formed on the upper glass leaving the adhesive surface free on the other side.

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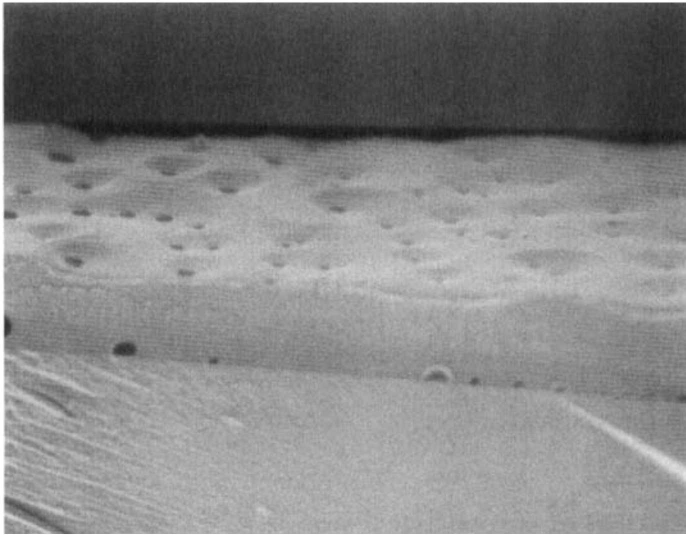

FIGURE 5 SEM micrograph of the adhesive surface after removing the substrate as shown in Fig. 4b. It shows blisters *ca.* 0.6 μm deep with a dark hole at their top (× 2000).

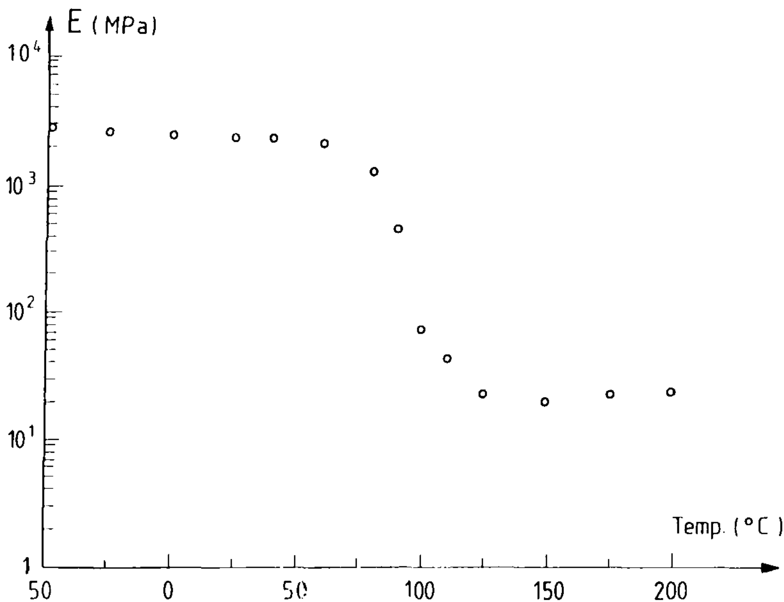

FIGURE 6 Above T_g, the adhesive elastic modulus drops to 20 MPa.

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It is known that voids are present in rubbers and that dissolved gases or liquids create bubbles of cavitation from these voids above a critical pressure[14] of $P_c = 5E/6$. In our case, where the epoxy's Young modulus is 20 MPa, the critical pressure amounts to $P_c = 16.6$ MPa. However, bubbles form along the interface and not in the rubbery material which implies that voids must exist along the interface and that it is only there that pressure above P_c develops.

The formation of blisters, from an initially debonded area of a solid membrane under a "blow off" pressure has been studied[15] and it was demonstrated that the height of the blister, h, was related to the pressure, P, by the equation

$$G = 0.65\ P.h$$

where G is the fracture energy of the membrane/substrate interface.

Considering that the adhesive interphase behaves as a membrane, the fracture energy of the adhesive may be deduced from the length of fracture of an adhesive bond cleaved by a wedge.[16]

In the case of the adhesive considered here, bonded to stainless steel, we found that the fracture energy was 100 Jm^{-2} in dry conditions and decreased to 8 Jm^{-2} when the joint was placed in high humidity (40°C, 90% RH).[17] Taking that value for G, a blister of 0.7 μm would occur at a pressure 16.6 MPa, as observed on the SEM micrograph (as the sample is inclined in the SEM our estimation of a 0.6 μm depth is in good agreement with the calculated value of 0.7 μm).

The origin of the pressure, P, could be the osmotic pressure developed by the dissolution of the superficial layer of the lower glass in the condensed water as suggested by Sargent *et al.*[18] Their estimation is that a pressure as high as 200 MPa can develop in saturated electrolyte solutions.

Actually, if the lower plate is replaced by sapphire or stainless steel no bubbles are observed in the time of the experiment. If copper is used as the substrate then bubbles appear again. Boerio[19] showed that copper is covered with a water-soluble CuO layer, which increases the pressure of water in the interfacial voids. This could explain why bubbles only occur along the soda lime microscopic slide and not along the upper tempered glass which is less soluble.

6. INTERFACIAL CRUMPLING

We have shown that weakening of the epoxy-amine adhesive bond occurs above 70% relative humidity and suggested that it comes from capillary condensation of water in small pores. We have not been able to prove the existence of such pores; however, we showed that voids must exist along the interface as blisters were produced in the adhesive when it is in its rubbery phase. This leaves another question open: why would voids form along the interface?

Many explanations may be offered, one referee of this paper suggested lack of molecular intimacy; however, we think that interfacial stress plays a role.

To make an adhesive bond, one uses a liquid and lets it solidify. During this process a strong contraction of the adhesive occurs. This leads, in turn, to high internal stresses along the interface and probably creates voids to release part of these stresses. This crumpling process may be observed on a film of adhesive in the following experiment. A film of adhesive (either hot-melt or B-staged epoxy) is bonded to a glass plate at moderate (80°C) temperature. Then the adhesive is coated with 3000Å of evaporated gold to form a glass-epoxy-gold joint. The gold surface is observed in the SEM and appears flat (Fig. 7a). Further, the adhesive is melted (case of a hot melt) or cured (case of a B-staged epoxy—shown in Fig. 7b) and the surface is observed again in the SEM. The crumpled gold is evident. We dared not to repeat this observation with a liquid epoxy-amine which could contaminate our evaporator. However, we think that the same process would occur.

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7. CONCLUSION: A MODEL FOR THE WEAKENING OF ADHESIVE BOND BY WATER

From previous results, the observations reported here and some hypotheses (that remain to be proven) we deduced the following model for the attack of adhesive joints by water (Fig. 8).

a) At relative humidities below 70%, the concentration of water in the adhesive is small and water remains bonded on polar groups of the polymer through hydrogen bonds between water and amino-alcohol.[7] The properties of the adhesive merely change.
b) Above 70% water condenses in pores and voids. The filling of voids along the interface lowers the adherence.
c) If a solute dissolves in the condensed water, osmotic pressure increases and may cause spontaneous delamination through coalescence of blisters.

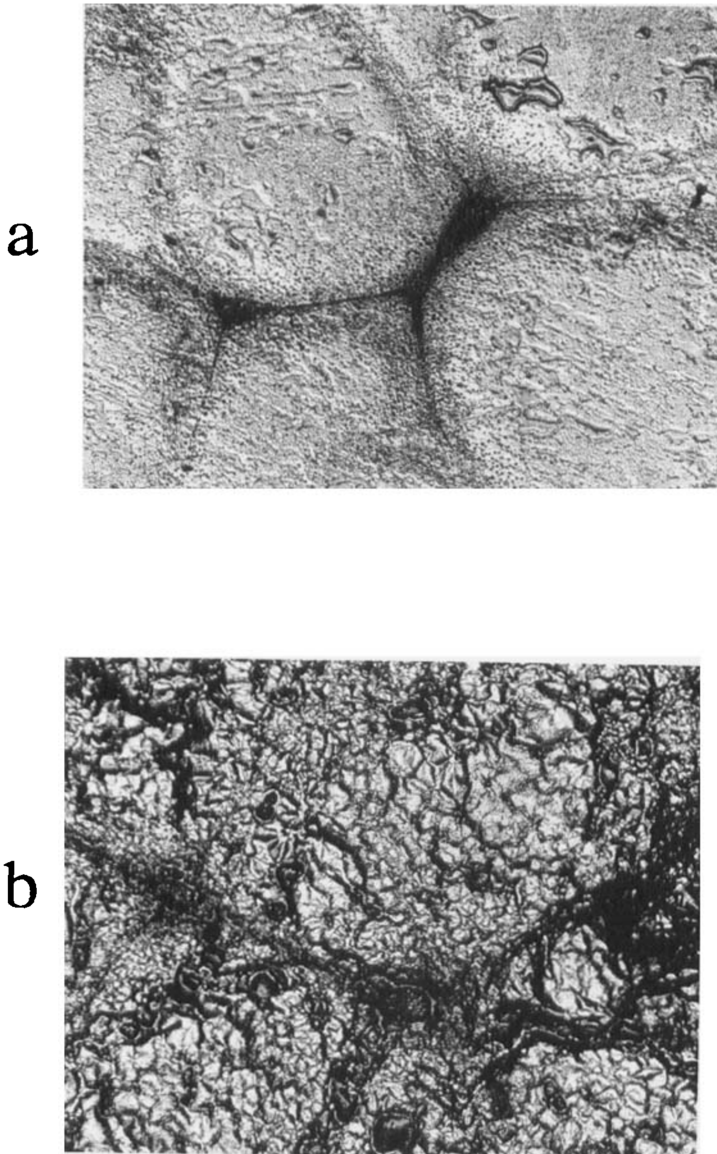

FIGURE 7 Surface of an adhesive film (B-staged epoxy) deposited over a glass slide, coated with gold: a) before curing; b) after curing: The gold layer has crumpled.

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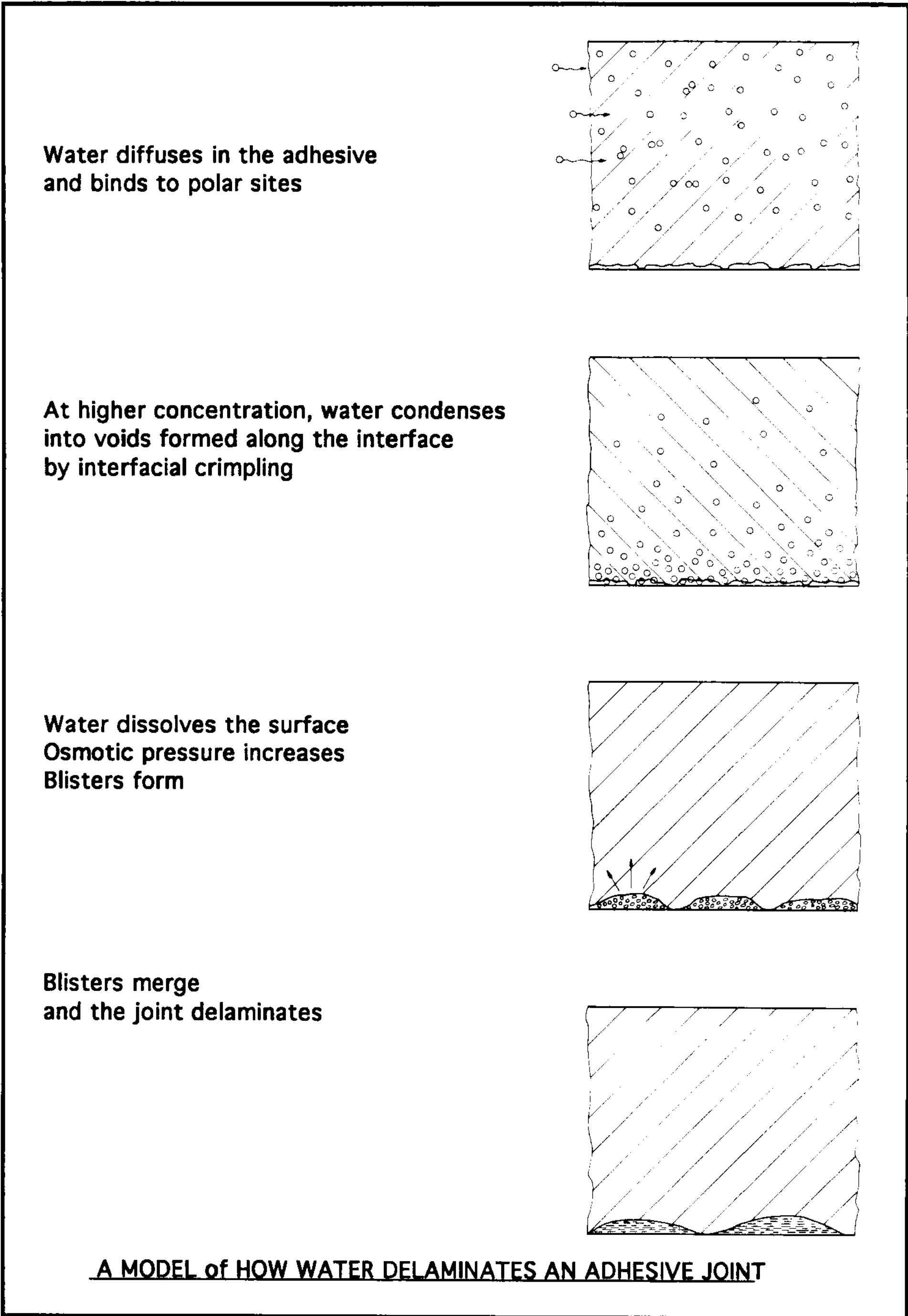

FIGURE 8 Model for water attack of adhesive bonds.

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