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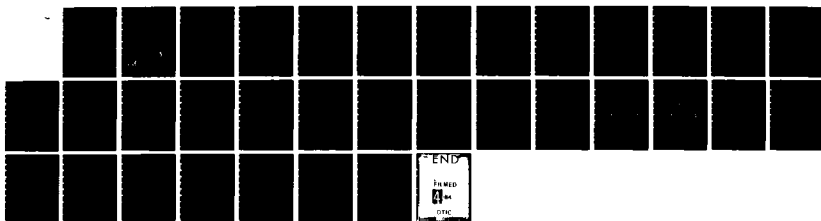
MOISTURE TRANSPORT IN COMPOSITES DURING REPAIR WORK(U)
NAVAL SURFACE WEAPONS CENTER SILVER SPRING MD J M AUGL
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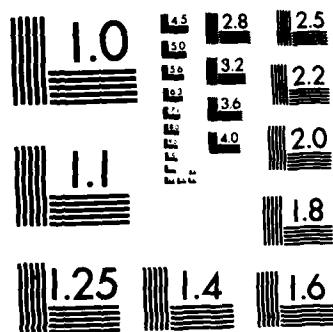
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MOISTURE TRANSPORT IN COMPOSITES DURING REPAIR WORK

BY JOSEPH M. AUGL

RESEARCH AND TECHNOLOGY DEPARTMENT

SEPTEMBER 1983

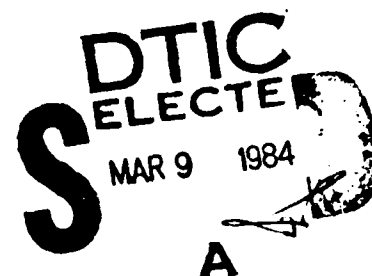
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↙ If the partial pressure of water dissolved in the still liquid adhesive exceeds the environmental (applied) pressure voids may form rapidly and reduce the load carrying strength of the bonded patch. An interactive desk top computer program was written for predicting the moisture profiles in the composite and the adhesive during the whole course of predrying and patch bonding. Thus it should be possible to get a better understanding of the problem and to obtain guidance for an experimental approach to optimize repair procedures. The underlying principles for the modeling are discussed and a specific example of moisture transport using a metal patch is given.

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Approved by:

JACK R. DIXON, Head
Materials Division



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CHAPTER 1

INTRODUCTION

The requirements for repair work on Naval aircraft composite wing skins that can be performed under depot conditions (or still worse, under field conditions) are quite restrictive. Equipment that can be used is rather limited as are the available repair space and time. The procedures must be simple enough so that they can be performed satisfactorily by personnel without special knowledge in composite materials technology. Repairs of small holes should not require more than perhaps a short predrying cycle (with heat guns) and a subsequent patch bonding using a heating blanket, held in place by applying a vacuum.

However, it has been observed during simulated experimental repair work that the glue lines frequently show a high content of pores and bubbles which are attributed to evaporation of moisture during the curing cycle. (Of course, other volatile materials such as residual solvents would act similarly). The purpose of this paper is to give some detailed analysis of the problem of moisture transport as a function of repair conditions. Although we have started an experimental program in this area, the present discussion will focus only on the underlying theoretical concepts. The theoretical model, for which we have written an interactive desktop computer program, is thought to aid in setting up a useful test program for optimizing the procedures of repair work.

CHAPTER 2

DISCUSSION

MECHANISMS OF BUBBLE FORMATION, GROWTH, AND TRANSPORT

It appears that the major source of bubble (void) formation during repair of composites is moisture. When the partial vapor pressure of the dissolved moisture (or any other dissolved species), in the still liquid adhesive, exceeds the confinement pressure of its surrounding, bubbles may form, grow, and migrate.

There are probably always a large number of entrapped air bubbles present that can act as nucleating sites and there are many active interfacial sites that can lead to bubble formation, thus the probability for nucleation is high enough and therefore will not retard bubble formation due to volatilization.

The growth of voids is governed by 3 effects: 1) The entrapped air will expand according to the ideal gas law. Thus at constant pressure the relative increase in void volume (due to entrapped gas) is directly proportional to the change in temperature; 2) An additional growth is given by the added partial vapor pressures of volatile components dissolved in the adhesive (which is a function of their concentrations, governed by Henry's law, and by their temperature dependence); and 3) By the confinement conditions. The term confinement condition is used here to combine all the effects that resist the expansion of a void. Obviously, this is a complex phenomenon that can not be easily calculated. It combines the applied external forces (for instance, the exterior pressure by the vacuum bag and the vacuum seen by the resin at its interface to air) and the integral of viscous forces that have to be overcome to move the confining liquid out of its way, which also includes surface tension effects of other voids that are pushed through narrow passages. One more and probably unimportant effect in the growth of bubbles is the coagulation of bubbles to form larger voids. This coagulation changes only the number of voids but not the void volume fraction.

To calculate effect 1 is trivial. Calculation of effect 2 is more difficult because it includes the rate of diffusion of volatiles into the bubble but can be done by numerical means. A calculation of the third effect appears to us rather hopeless. A recent discussion on that subject has been presented by Kardos et al.¹ We believe it might be possible to approach it experimentally

¹Kardos, J. L., and Dudukovic, M. P., "Void Formation and Transport during Composite Laminate Processing," ACS Paper presented at Kansas City, Organic Coatings and Applied Polymer Science Proceedings, Sep 1982, p. 639.

by actually measuring the force necessary to push an adhesive at a given temperature through a model adhesive patch. (Thus, the integral forces are actually measured rather than calculated.)

Knowledge of all three effects mentioned above would probably suffice to estimate under which circumstances one reaches the critical conditions for rapid void generation and growth; i.e., sufficient conditions for void formation and growth.

However, it is not only considerably easier to estimate the necessary conditions for accelerated void growth, but also, in considering the necessary conditions only, one is automatically on the safe side which is more desirable anyway for practical applications.

NECESSARY CONDITIONS FOR RAPID VOID FORMATION

Since the increase in void volume (due to thermal expansion of entrapped air voids) is only linear with increasing temperature this effect is a simple superposition and shall not be considered here.

The necessary conditions for void growth therefore assumes that the viscosity effect is negligible compared to the pressure generated inside the void. This leaves us with the simple measurement of the equilibrium partial pressure of the volatile species (moisture, etc.) as a function of temperature and of its concentration (activity) in the adhesive, i.e., a determination of the sorption isotherm. This defines whether the vapor dissolved in the adhesive will tend to desorb into the void or not.

The concentration of moisture in the adhesive will change if moisture diffuses out of the heated composite into the adhesive or out of the adhesive into the applied vacuum.

Therefore we have, in essence, to deal simultaneously with the problem of volatility (vapor pressure of dissolved moisture) and of moisture transport as a function of applied pressure, temperature and concentration. The two important concepts to consider are therefore the sorption isotherm and a transport equation for moisture.

SORPTION ISOTHERMS

Sorption isotherms (or the equilibrium concentration between moisture dissolved and moisture in the gas phase) is usually given in the form of Figure 1, where ϕ is the weight (or volume) fraction dissolved, a = moisture activity, p = partial vapor pressure, p_0 = saturation pressure above pure water ($p \cdot 100/p_0$ is usually called relative humidity). This means that at a given relative humidity the immediate surface of the absorbent will be in equilibrium with its surrounding vapor (for all practical purposes instantaneously). The question of whether the diffusion of vapor is outward or inward is given by the concentration gradient in the interior of the sorbent and not by the average concentration. Thus, it is the boundary condition (which may change rather quickly) that will determine the net flow through the surface in a given time. The rate of flow is given by the slope, i.e., the moisture gradient.

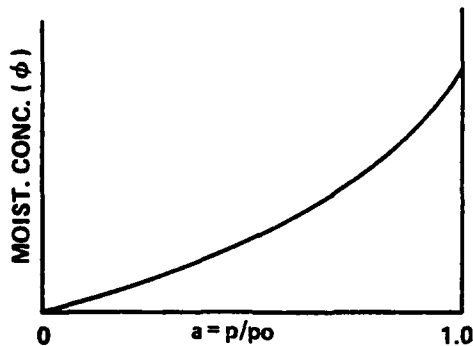


FIGURE 1. (U) SORPTION ISOTHERM

In conjunction with the sorption isotherm one has to consider the vapor pressure curves as shown in Figure 2. The top curve of Figure 2 shows the vapor pressure curve of pure water as a function of temperature (i.e., 100 percent relative humidity). The other curves show the partial vapor pressures for the indicated relative humidities.

As an example let us say we had fully equilibrated a liquid adhesive at 60% RH and we would heat it (at 760 mm Hg=atmospheric pressure) then we would not expect to see bubbles form until the temperature has reached 115°C (not 100°C) as can be seen from Figure 2. If we had applied a vacuum of 10 mm Hg we might expect bubble formation as low as 19°C (slightly below room temperature). Note, these are only the necessary conditions; whether bubble formation really occurs depends on the total dynamics given by the sufficient conditions.

The relative humidity in the gas phase can change rapidly with temperature. Example, see Figure 2: assuming we had 60% RH at 20°C this corresponds to 10^{-5} g H_2O/cm^3 of water in air (intersection 20°C with 60% RH curve). Heating this gas to 100°C (go horizontally to the right until intersecting the 100°C vertical) one can see that the RH is between 1 and 2.5. A reduction in pressure at constant temperature will have a similar effect (going down vertically on the same diagram). Thus, by using this diagram or an analytical representation of it one can easily determine the boundary conditions at each time step during the cure (the computer code uses a third degree polynomial subroutine to calculate the respective boundary conditions).

MODEL FOR A NUMERICAL APPROACH OF SOLVING THE DIFFUSION PROBLEM

For estimating the simultaneous transport of moisture in the composite and in the adhesive patch we believe that Fick's diffusion equation is suitable if there is a predrying step involved which removes quickly the moisture from the open pores, cracks and fiber debonds which have either existed in the virgin composite or which were caused by the normal aging in service or, more likely, which were generated as a result of the damage. A preheating step is not only beneficial in removing entrapped moisture in open pores but also it will reduce the rate of moisture flux through the surface per unit time. It may not be necessary to remove all or even most of the moisture in a composite that is to be repaired, it is sufficient to reduce the rate of flux such that it will not

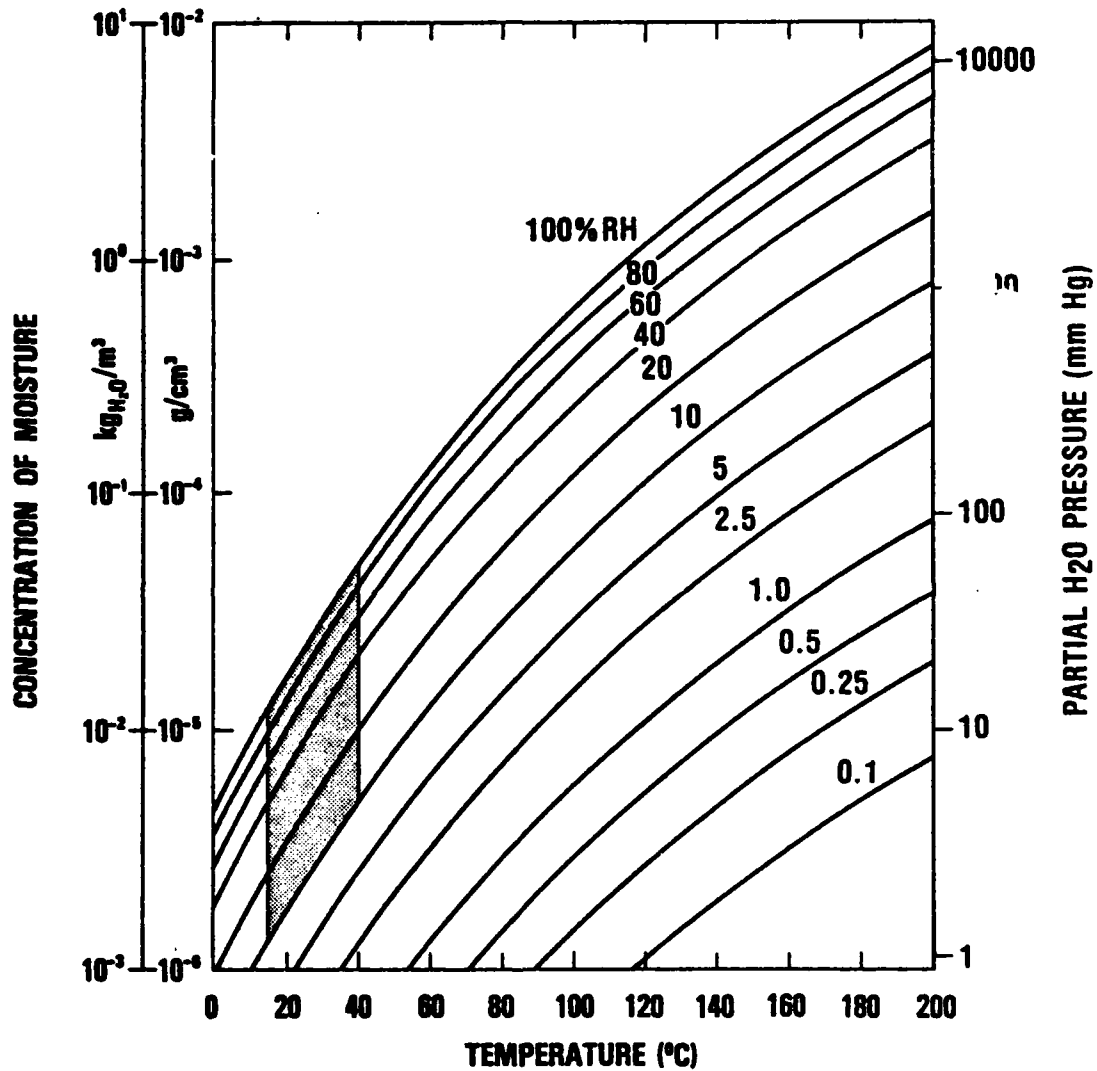


FIGURE 2. (U) MOISTURE CONCENTRATION IN HUMID AIR AS A FUNCTION OF TEMPERATURE FOR DIFFERENT RELATIVE HUMIDITIES

exceed the critical, "necessary conditions" for bubble formation in the adhesive during the curing process or until the adhesive has reached at least the gelation point where it is no longer fluid.

For modeling the moisture transport we will use a finite difference approach, changing the Fickian equation to a finite number of linear algebraic equations that can be solved by a simple matrix inversion. In addition it is necessary to specify boundary conditions and curing conditions (which will govern the change in boundary conditions and diffusion coefficients). The following subsections will discuss some details of the modeling which includes boundary conditions, curing conditions and other required input data, and finally, a specific example is considered where a metal patch is thought to be bonded to a carbon fiber composite.

FINITE DIFFERENCE EQUATIONS

Since the thickness of the composite plate to be repaired is small compared to the overlapping distance of the patch the problem of moisture transport by diffusion becomes essentially one-dimensional (away from the edges of the patch or the composite). Fick's equation (1) can be replaced by the finite difference equations (2).

$$\frac{\partial M}{\partial t} = D(T, M) \frac{\partial^2 M}{\partial x^2} \quad (1)$$

$$\frac{M_i^{n+1} - M_i^n}{\Delta t} = \frac{2D(t^{n+1})}{\Delta_i + \Delta_{i+1}} \left[\frac{M_{i-1}^{n+1}}{\Delta_i} - \left(\frac{1}{\Delta_i} + \frac{1}{\Delta_{i+1}} \right) M_i^{n+1} + \frac{M_{i+1}^{n+1}}{\Delta_{i+1}} \right] \quad (2)$$

In equation (1) M = Moisture concentration in ml H_2O per unit volume (ml) of composite or adhesive. (Note: For consistency the weight percent values are internally converted into volume percents via densities of adhesive and composite.) T = Temperature ($^{\circ}K$), t = time (sec), x = distance (cm) into the composite and adhesive, D = moisture diffusion coefficient (cm^2/sec).

In equation (2) Δt = time step (sec) Δx_{i+1} = finite distances in the x -direction, the subscripts i and $i+1$ in M represent the spatial points and the superscripts n and $n+1$ the points at the n^{th} and $n+1^{st}$ time steps, $D(t^{n+1})$ is the diffusion coefficient at the $n+1^{st}$ time step.

Since the structure of the linear system of equations is quite similar to those we discussed previously in connection with modeling moisture diffusion in an outdoor environment we wish to refer to the respective report² rather than repeat the extended derivation. Suffice it here to say that the system of equations gives a tridiagonal matrix which upon decomposition into upper and lower triangular matrix is particularly easy and fast to invert with a computer.

INITIAL AND BOUNDARY CONDITIONS

To solve a general problem as indicated in Figure 3, it is necessary to consider five different boundary situations shown in Figure 4. The patch in Figure 3 can be either a composite or a neat adhesive, the bleeder cloth may be replaced by a metal sheet (thus providing a metal patch), the cover has the purpose of holding the patch in place by means of an applied vacuum. The honeycomb structure on the opposite side may be perforated to release the generated pressure, or may be closed, retaining the enclosed air and moisture which may develop a considerable internal pressure. Figure 4 shows the following boundary conditions: a. Composite/air; b. composite/closed cavity; c. composite/adhesive patch; d. adhesive/metal; e. symmetric condition (interior). Boundary condition e is actually the same as d.

Since the solubility of moisture in the composite is probably different from that of the adhesive it is necessary to introduce a distribution coefficient at this interface (boundary condition c) which governs the concentration on each side of the interface. This distribution coefficient $K_c = C_c/C_a$ is the ratio of moisture concentration in the composite to that in the adhesive (in terms of weight percent). Again, this is internally converted with respect to volume percent $K_d = K_c * \rho_c / \rho_a$.

In order to solve the diffusion equation one needs to know the initial distribution of the diffusant (moisture) in both the composite and the adhesive patch.

It is obviously not easy to determine the internal moisture distribution in the composite since this depends on its previous history. However, in the absence of specific data it suffices to assume the worst condition that one might find in a realistic environment, then at least, one is on the conservative side of the prediction. (These and other assumptions will be discussed in the following subsection.) The concentration of moisture at the surface (or interface) and the diffusion coefficient (as a function of temperature) determine the rate of change of concentration in the interior. Thus, the sorption isotherms for both, the adhesive and the composite have to be known as well as both diffusion coefficients and the temperature profiles of predrying and subsequent curing. If the room temperature RH is known for both the surrounding air and that in the honeycomb cavity (worst case, closed) then the RH changes with temperature and/or applied vacuum are easily calculated from the

²Augl, J. M., and Berger, A. E., The Effect of Moisture on Carbon Fiber Reinforced Composites. III Prediction of Moisture Sorption in a Real Outdoor Environment, "NSWC/WOL/TR 77-13, Jun 1977, p. 13.

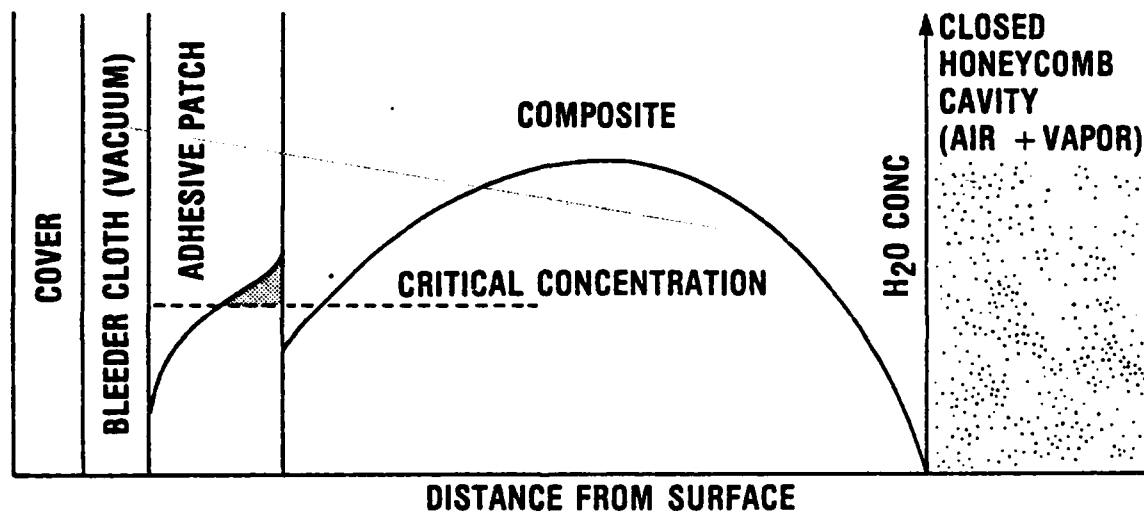


FIGURE 3. (U) SCHEMATIC OF A MOISTURE PROFILE AT SOME TIME DURING THE ADHESIVE PATCH CURE

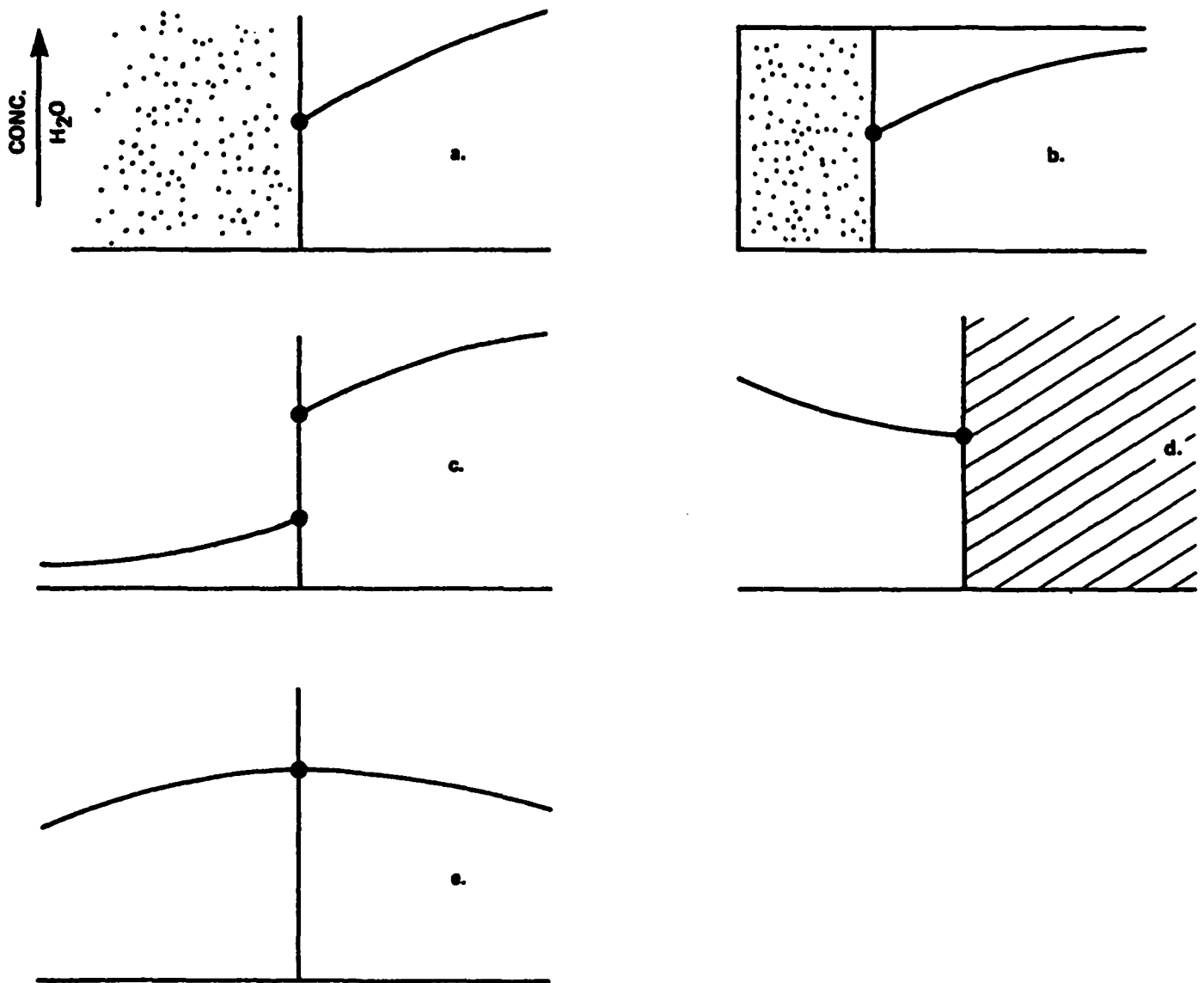


FIGURE 4. (U) BOUNDARY CONDITIONS DURING DRYING AND CURING

steam table (given in Figure 2) which is done by a subroutine in the program. Moisture will diffuse into the adhesive and into the honeycomb cavity. The change in mass of water in the cavity and the combined pressure increase of air and vapor in the cavity is also calculated in a subroutine.

It appears that the initial condition of the moisture concentration in the adhesive should be easier to establish since it is the result of a controllable fabrication process. If the adhesive patch is prefabricated and sealed, or if the adhesive fluid is well sealed before use, one may expect that it will not exceed a preestablished maximum moisture concentration. The lower that is the better, because it then has a larger capacity to sorb additional moisture before bubbles may form. During this time the adhesive may have gelled and will exert a much higher resistance to bubble formation, even when the necessary conditions are exceeded.

REASONABLE FIRST APPROXIMATIONS FOR MATERIAL PARAMETERS

The following input data are required for solving the diffusion equation: a. Sorption isotherms of the composite and of the adhesive. (This establishes at the same time the distribution coefficient at the interface between composite and adhesive.); b. Diffusion coefficients as a function of temperature (and possibly of concentration) for both the adhesive and the composite; c. The initial moisture distributions in the adhesive and in the composite; d. The temperature profile of the predrying and curing schedule; e. The applied vacuum during the curing procedure. An accurate knowledge of all these data may be desirable but they are most likely unavailable in practical repair work. Thus, the question is: can one reasonably estimate the "necessary conditions" for bubble formation under prescribed predry and curing conditions?

The answer is that one can estimate a conservative, safe limit in time and temperature or any combination thereof by assuming "worst conditions".

In a previous investigation^{3,4} we showed that it may take a very long time until the interior of a composite is in equilibrium with the average moisture level of its surrounding. Also, there are only very few places on the surface of the earth and sea where the average relative humidity exceeds 80%. Therefore, the assumption that the composite to be repaired has a uniform concentration that is in equilibrium with a surrounding of 80% RH may, for all practical purposes, be considered as a worst case. Thus, in the absence of better information, we will take this value in order to be on the safe side.

For many polymers, rubbers and epoxy resins the sorption isotherm up to 80% RH is fairly linear so that the moisture concentration may be represented by $C = \gamma \text{ RH}$ (where γ is a constant). (Of course any shape of the sorption isotherm can be approximated satisfactorily by a third or fourth degree polynomial if necessary.)

³Augl and Berger, Moisture. III, Jun 1977.

⁴Augl, J. M., and Berger, A. E., The Effect of Moisture on Carbon Fiber Reinforced Composites. I Diffusion, NSWC/WOL/TR 76-7, Sep 1976.

For instance, the moisture equilibrium in Hercules 3501-6 epoxy resin at 80% RH is 3.76% (by weight) and for the composite with 0.62 fiber volume fraction it is 1.18%. Also, it appears that the sorption isotherm is not too strongly dependent on the temperature.^{5,6} Thus the temperature dependence of the sorption isotherm, may in a first approximation be taken as independent or at worst linear with temperature.

For many epoxy resins the temperature coefficient of the diffusivity (i.e., the activation energy of diffusion) is about the same⁵ though the absolute values may differ within an order of magnitude between 10^{-9} to 10^{-8} cm²/sec. Using a finite difference method⁵, we obtained the change in composite diffusion coefficient as a function of fiber volume fraction which was in good agreement with experimental measurements. For carbon fiber lamina of a volume fraction of 0.62 the diffusion coefficient is about 23% of that of the neat resin matrix. The temperature coefficient in composites is the same as that of the matrix (if there is no appreciable diffusivity in the fiber itself). The program uses the diffusion coefficient for Hercules 3501-6 and its temperature coefficient as default values (which can be easily changed if necessary). It also appears that, for a number of polymer systems,⁶ the temperature coefficient of the moisture diffusion coefficient is the same below and above glass transition temperature. Whether this behavior also extends into the ungelled state is not explored. However, as a first approximation it was taken to be such. (Experimental measurements are planned to investigate this assumption.)

CONVERGENCE OF THE METHOD

One of the questions in using differences instead of differentials is obviously the convergence as a function of time and space differences.

Figure 5 shows the calculated interior moisture distribution through half the composite after 10 hours drying time using 1, 2, 4, 10, 20, 40 and 100 time steps. This figure shows that 10 time steps seem quite adequate for practical purposes. The same absolute time step does not give equally good convergence for different times (see Figure 6) where 360, 720, and 1500 sec were used as time steps to calculate the internal moisture distribution after 1 and 10 hours drying time. In order to obtain an equally good time step which is independent of composite thickness we used arbitrarily a 1/2000 of the time necessary to reach 97% of the equilibrium concentration. This time we call quasi equilibrium time. (Why not wait until the system is at 100% equilibrium? Because it takes infinitely long to get to that point.) The quasi equilibrium time is given by $t_{eq} = 1.5 \cdot h^2 / D$ and therefore $\Delta t = 1.5 \cdot h^2 / (2000 \cdot D)$. This time step assures good convergence for all practical time intervals of interest (it is automatically chosen by the program and may be changed manually if so desired in order to obtain simple printout time intervals).

⁵Augl and Berger, Moisture. I, Sep 1976.

⁶Stannett, V., and Williams, J. L., "The Permeability of Poly(ethylmethacrylate) to Gases and Water Vapor," J. Pol. Sci. Part C, No10,45 (1965).

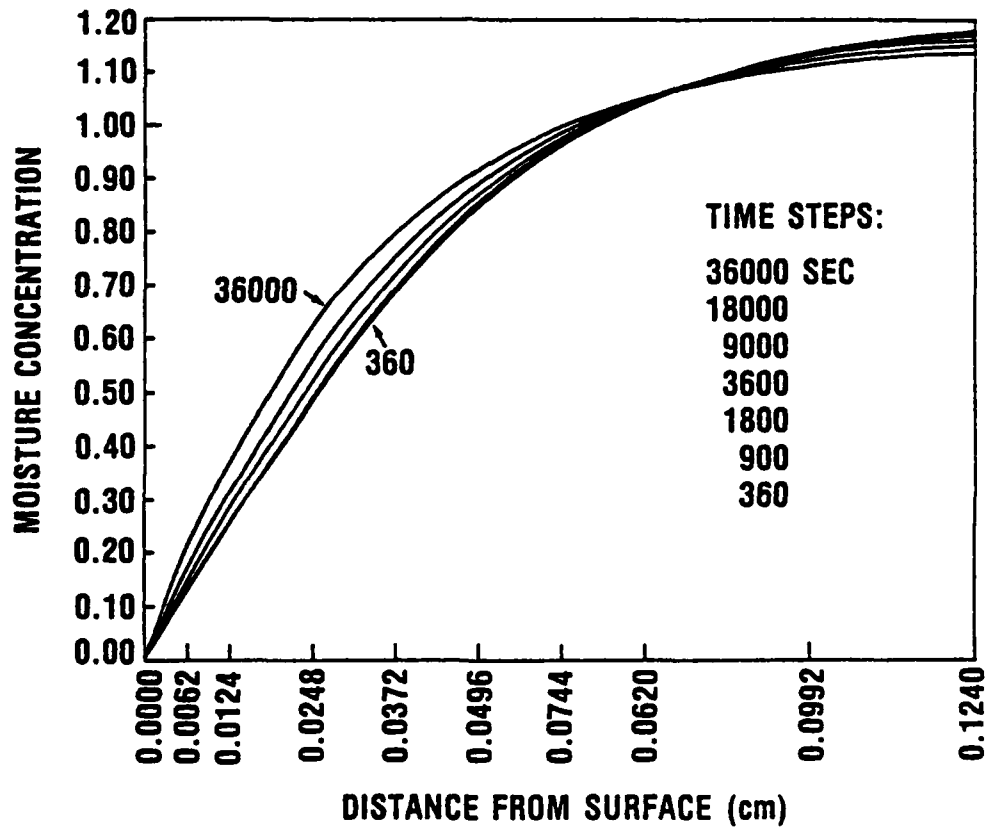


FIGURE 5. (U) CONVERGENCE OF FINITE DIFFERENCE METHOD USING DIFFERENT Δt

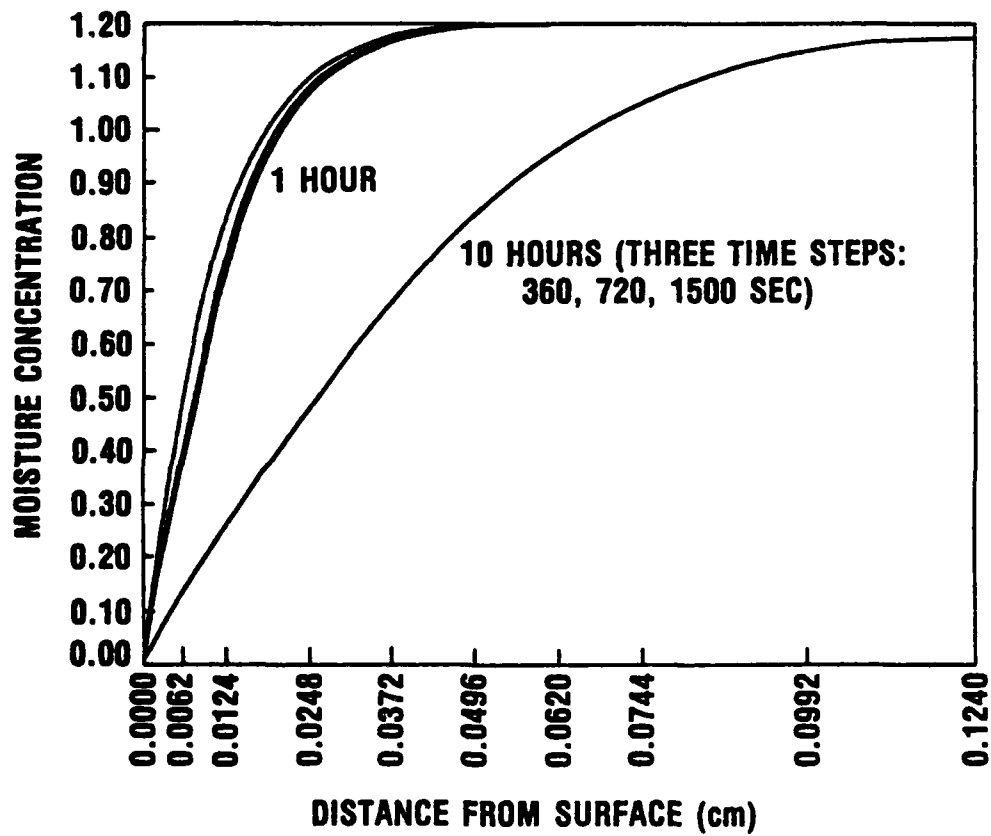


FIGURE 6. (U) CONVERGENCE OF FDA METHOD FOR SAME Δt BUT DIFFERENT TIMES

SPECIFIC EXAMPLE

Since it may lead to a better understanding of the discussion we want to run briefly through a specific example.

We will consider a 3501-6/AS carbon fiber epoxy composite plate (since we have studied the sorption and diffusion behavior of this resin in some detail⁷). The plate is to have a thickness of .248 cm and is to be repaired with an adhesively bonded metal sheet. The glue line shall be 0.01 cm, and the initial moisture concentration in the adhesive be 0.1%. The opposite side of the composite plate is a closed honeycomb structure which we assume to confine the moisture (worst case). The composite shall be predried for 2 hours at 150°C with heat guns. After this predrying step the metal/adhesive plate is bonded to the composite. The applied vacuum is 500 mm Hg. The temperature is raised to 121°C at a rate of 2°C per minute, held at this temperature for 45 minutes, then the temperature is increased to 177°C at a rate of 2° per minute. The final hold time at this temperature is 120 minutes.

The limited time for predrying can obviously not remove all the moisture in the composite. To do that would require times as long as those shown on Figure 7 where the times to remove 97% of all the absorbed moisture is shown as a function of composite thickness and drying temperature.

Another question which is frequently asked is, whether it is possible to shorten the drying time significantly if, in addition to heat, vacuum is also applied to the composite. The perhaps surprising answer is no. Figure 8 shows the difference in internal moisture concentrations after 10 hours drying time for different temperatures with and without use of vacuum. Only at 70°C the graph resolves two slightly different curves. At 100°, one can barely resolve the difference and at higher temperatures it can not be seen. The reason is simple. The surface equilibrium is given by the surrounding RH which decreases rapidly with increasing temperature and therefore vacuum has little additional effect on the internal gradient.

Therefore a reasonable predrying time of two hours was chosen. The change of the internal moisture distribution after 30, 60, 90 and 120 minutes is shown in Figure 9. Figure 10 shows the moisture distribution in the adhesive and in the composite at 30 minutes time intervals during the indicated curing schedule.

The corresponding critical concentrations not to be exceeded were given (in weight %) as: 4.89, 1.67, 1.67, and 0.37 up to the end. Looking at the concentration profiles in the adhesive (see Figure 10) one can see that the first 3 time steps are not exceeding this critical limit but as the ultimate cure temperature is reached (between 1.5 and 2 hours) the sorbed moisture

⁷Augl, J. M., Moisture Sorption and Diffusion in Hercules 3501-6 Epoxy Resin, NSWC TR 79-39, Mar 1979.

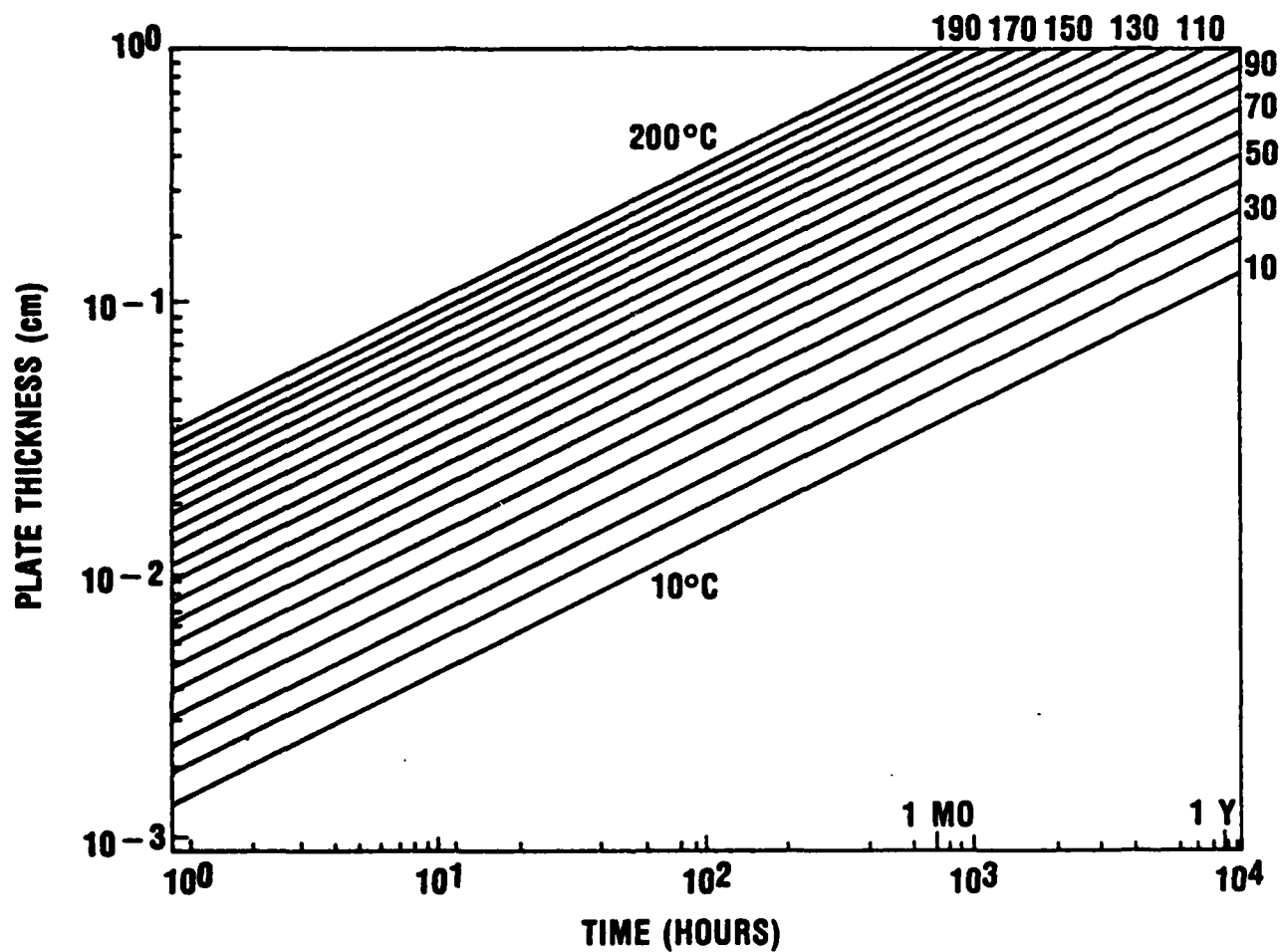


FIGURE 7. (U) SORPTION TIMES TO 97% OF THE EQUILIBRIUM CONCENTRATION FOR A COMPOSITE WITH $V_f = 0.62$ (3501-6 RESIN/CARBON FIBER)

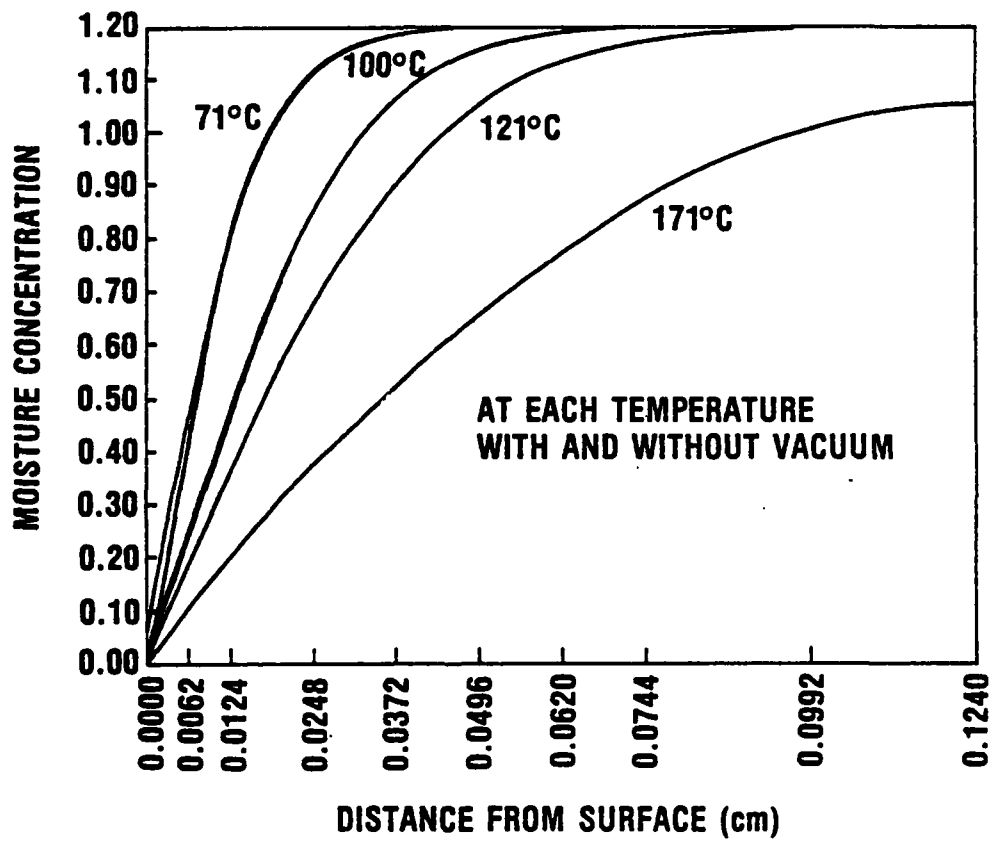


FIGURE 8. (U) EFFECT OF DRYING WITH AND WITHOUT VACUUM (10 HRS)

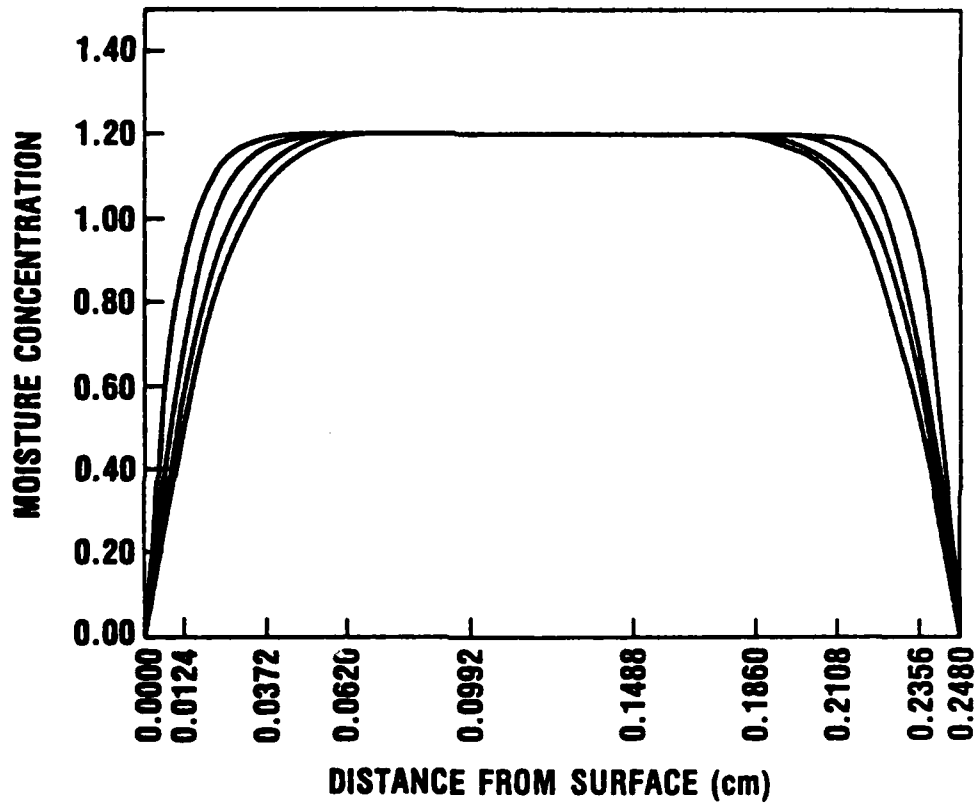


FIGURE 9. (U) MOISTURE DISTRIBUTION IN THE COMPOSITE AFTER 30, 60, 90 AND 120 MINUTES (WITH A UNIFORM 1.2% DISTRIBUTION AT TIME ZERO)

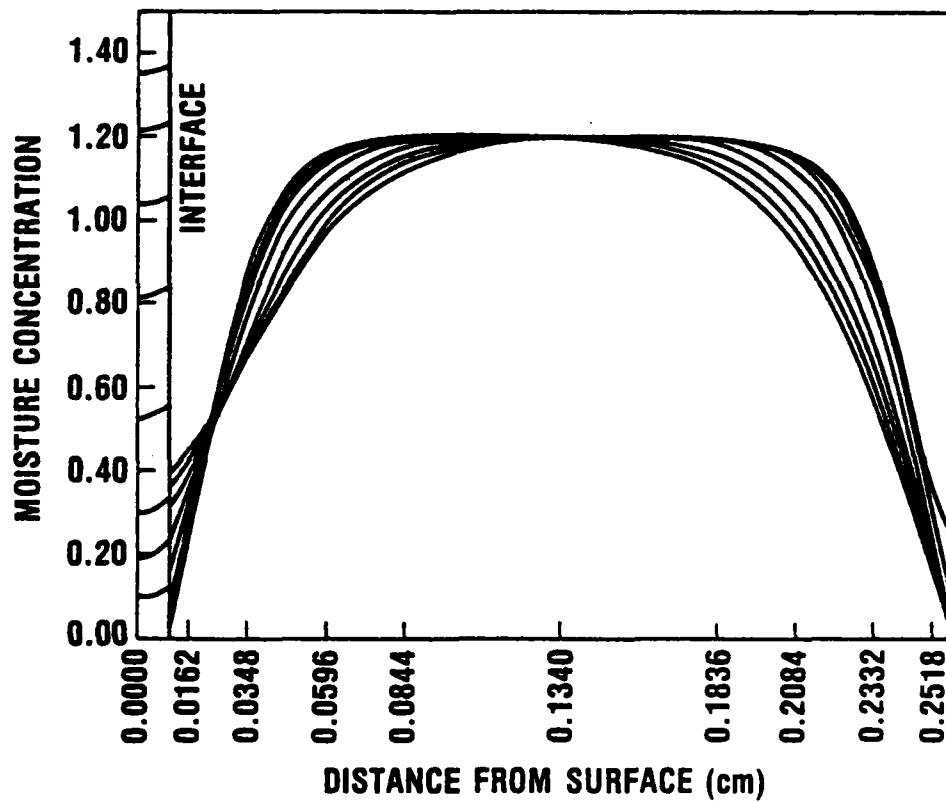


FIGURE 10. (U) MOISTURE DISTRIBUTION (IN 30 MIN. INTERVALS) IN THE COMPOSITE AND IN THE ADHESIVE DURING THE PATCH BONDING PROCESS. (USING A PREDRIED COMPOSITE)

exceeds the critical concentration which may lead to bubble formation unless the adhesive has sufficiently gelled in the meantime to prevent void expansion and transport. If there is no predrying step, the moisture pickup in the adhesive is much higher per unit time as can be seen on Figure 11 (where the fifth moisture distribution line is already out of plotting range). Although the first hold temperature (121°C) remains still in the safe range (below 1.67%).

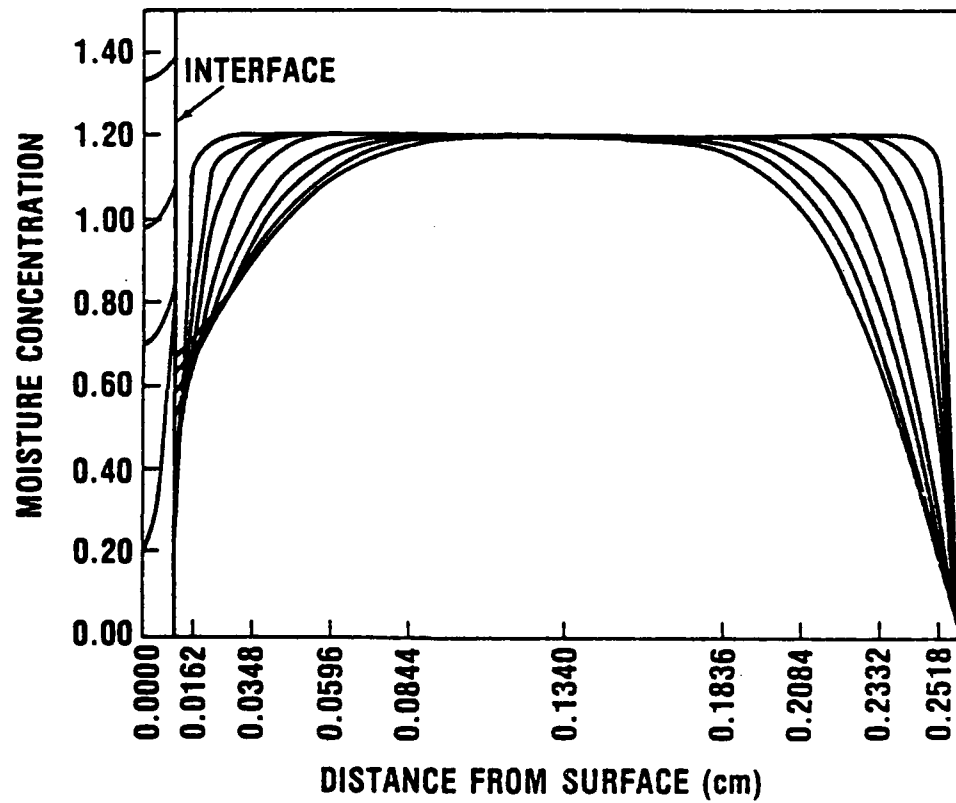


FIGURE 11. (U) MOISTURE DISTRIBUTION (IN 30 MIN. INTERVALS) IN THE COMPOSITE AND IN THE ADHESIVE DURING THE PATCH BONDING PROCESS. (WITHOUT PRIOR DRYING STEP)

CHAPTER 3

CONCLUSIONS AND CONSIDERATIONS FOR OPTIMIZATION

1. The "necessary conditions" for bubble formation in an adhesive during patch cure have been discussed on the basis of sorption isotherms and vapor pressure curves. Fick's diffusion equation together with the changing boundary conditions (which are governed by the predrying and curing procedures) allow one to calculate the moisture distributions in the adhesive and in the composite at all times, and therefore, to estimate the critical conditions for bubble formation.

Partial predrying of the composite is useful in two respects: it removes entrapped moisture from open cracks and it reduces the rate of flux into the adhesive.

2. It will be useful to gel the adhesive at a temperature such that the "critical concentration" of moisture (which is a function of temperature and applied pressure) is not exceeded.

3. Application of vacuum should be reduced to a minimum. Bubble formation increases strongly with the applied vacuum if the adhesive has access to the vacuum as can be readily seen in Figure 12.

4. A chemical approach to quench moisture during the curing process (such as the use of a carbodimide additive to the adhesive) which may prevent bubble formation should be investigated.

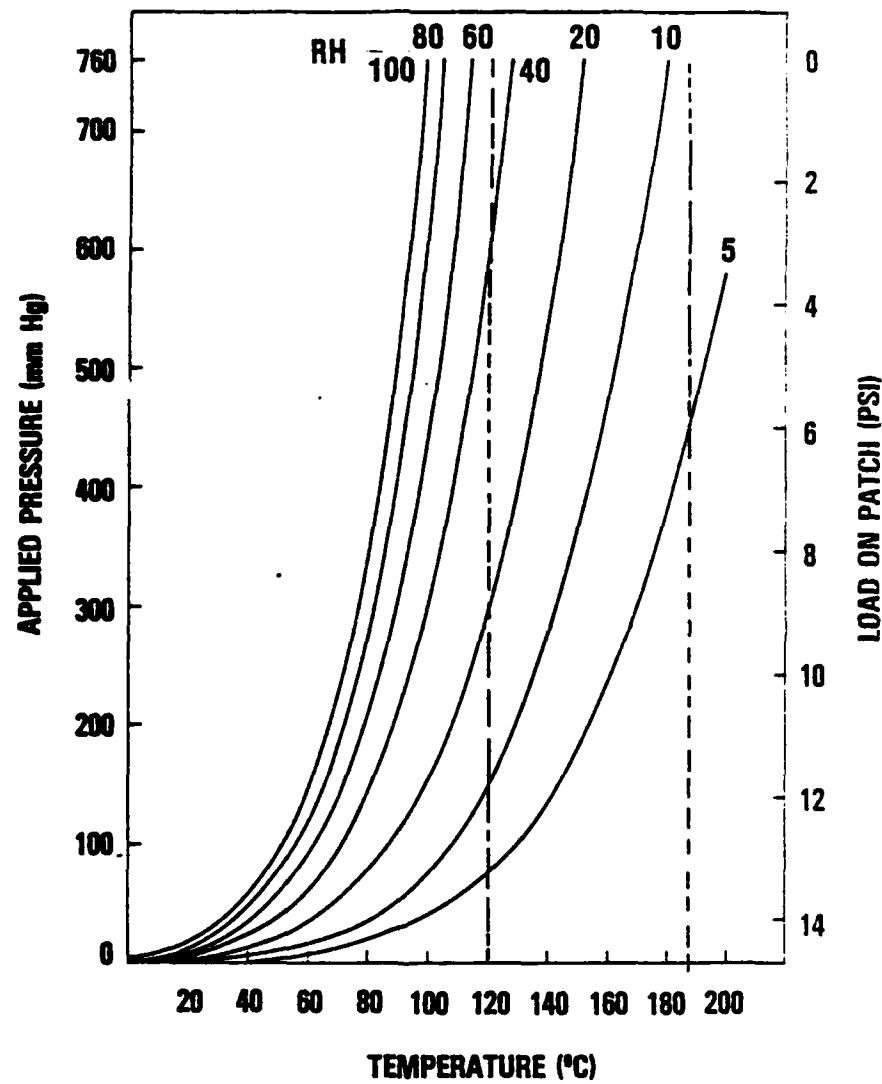


FIGURE 12. (U) EQUILIBRIUM PRESSURE OF WATER VAPOR AS A FUNCTION OF TEMPERATURE FOR DIFFERENT RELATIVE HUMIDITIES

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