

# Effects of Temperature-Humidity Variations on the Formation of Voids in V-22 (Osprey) Blade and Spar Assemblies

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December 2004

## **Introduction**

It is well known that the occurrence of voids during manufacturing of 901 (V-22) Blade and Spar Assemblies has become a major defect problem and cost driver affecting the overall efficiency of the production process. One of the areas assigned for further investigation was the possible role that day-to-day, month-to-month and seasonal floor environmental temperature and humidity levels played in the formation of voids. Several workers had noted a seemingly higher occurrence of voids during the hot summertime months than during cooler winter periods. While specific causes directly attributed to void formation are poorly understood, there has been an underlying suspicion that higher humidity levels in the shop environment played a significant role in their occurrence.

The purpose of this quick study was to evaluate historical temperature and humidity data for the 901 Blade and Spar assembly area and determine if possible correlations might exist regarding the formation of voids detected within the bodies and bonding interfaces of those assemblies. To kick off the project, daily shop floor relative humidity and air temperature data were manually tabulated from shop floor chart recorders and reviewed for the period January 1, 2003 through September 13, 2004. This data was used to estimate the corresponding water vapor pressures and dew point temperatures (using the Magnus-Tetens model) which permitted the comparison of void failure dates and rates to a single environmental variable.

Concurrently, historical QMS data was accumulated and reduced covering all void defect citations generated for the 901 Spar (Molded), Blade Assembly and Spar Assembly <sup>(1)</sup> for the period January 1, 2003 through September 13, 2004. These results permitted direct correlations to be attempted regarding void failure rates and relevant shop conditions over the time period of interest. The intent was to compare temperature and humidity levels for parts generating void-related QMS documents with those dates and time periods corresponding to 'good' parts. Results from this activity are presented in the Analysis section.

In addition to identifying possible correlations between void failure rate and humidity-temperature levels, there was an underlying goal to better understand the materials and processes in the 901 Blade, Spar and Spar Assemblies and to identify potential causes or effects that might be associated with voids. An effort was made to research and present the major mechanisms that might be associated with the interaction of environmental variables and some of materials used during the assembly process, particularly, the film adhesive AF-163 produced by 3M. This analysis is presented in the Discussion section.

## Summary

Results from this study could not completely validate the perception that void failure rates were directly or consistently related to *seasonal* temperature-humidity variations. However, the results do indicate that correlations exist throughout the year, between humidity levels and void failure rates for the Blade Assemblies (901-015-301-115/116) and Spar Assemblies (901-015-303-101B/102B). As anticipated, higher humidity levels tend to correspond to higher void failure rates for both the Blade and Spar Assemblies. The same cannot be said for the Molded Spar assembly where no distinctive correlation could be drawn and thus, the results were deemed inconclusive. For Blade and Spar Assemblies, void failure rates can be characterized in terms of shop floor relative humidity values using regression analysis with correlation fits ( $R^2$ ) in the 0.7 – 0.9 range. For the Molded Spar, only a scatter plot was obtained and no correlation fit could be documented.

Average air temperature variations throughout the period were less than about 5 or 6° from nominal, and seemingly played little or no role in the void failure rate. Initially, it was deemed necessary to evaluate the dew point temperature and associated water vapor pressure to determine their importance in relation to the standard relative humidity levels recorded in the shop area. Plotted results of estimated water vapor pressures and dew point temperatures illustrate the fact that these two parameters, as well as the relative humidity, are all a measure of the same property - the air water content. While vapor pressure and dew point were interesting to estimate and plot, they provide little insight above and beyond that given by the Relative Humidity.

Since all voids in the Blade and Spar Assemblies appear to occur within the bondline (AF-163 interface medium), the most likely mechanism involves absorption of atmospheric moisture into the uncured adhesive via a diffusion process. Incorporation of absorbed moisture within the material is believed to occur by hydrogen bonding of absorbed water molecules with pendent hydroxyl groups along the uncured polymer network, particularly those hydroxyl groups attached to phenolic rings in the epoxy-phenolic resin blend, until upper cure temperature (or gelation) is reached when the water molecules begin to volatilize. Segregation of the water molecules from the resin gel is followed by localized concentration of water vapor pockets, and as the gaseous water molecules escape from the hardening resin, casted voids inevitably remain behind.

## Analysis

Initial activities of this task involved acquiring and grinding through raw data contained in the shop floor temperature and humidity charts, as well as all QMS documents generated as a result of *out-of-spec* voids for the period Jan 1, 2003 – Sep 13, 2004. Attempts were made to identify the exact day(s) that each part was at the specific process(es) believed to be related to the formation of voids, i.e... for *Molded Spars* - the day Spar Caps and torque wrapping were being installed into the mold; for *Spar Assemblies* – the day the Abrasion Strip Assembly was being bonded to the Spar and/or the day the Nose Cap, Abrasion Strip and Heater Blanket were being bonded together; for *Blade Assemblies* – the day the Blade Skins were being joined to the Core and Spar Assembly surfaces. Identification of the specific process dates throughout the year 2004 was time consuming but generated fairly confident results which were used to derive average time factors. Most of the 2003 information had been purged from the QMS system and so the average time factors were required to generate *likely* process dates for parts made in 2003. Ironically, some parts may pass through the entire manufacturing sequence in a few days, others may take weeks or months due to unforeseen problems. Obviously, being limited to the use of time averages to determine process dates can incorporate undesirable errors into the results.

Current environmental requirements for the A&R work area are called out in BPS 4458: “The temperature shall be maintained between 65°F and 80°F and shall be continuously monitored and recorded. The relative humidity shall not exceed 60 percent and shall be continuously monitored and recorded. Under emergency conditions, temperatures up to 85°F and relative humidity up to 65 percent shall be permitted. Emergency conditions are defined as equipment failures or bond repairs that cannot be made in a controlled area. The deviations in temperature and humidity controls permitted shall not exceed 4 hours in a 24 hour period, nor shall adhesives, or primers, be exposed to such environments more than twice in a 7 day period.”

The heating/cooling system in the 901 assembly area is several decades old (there is word it is to be upgraded in the near future). Unfortunately, every time an operator needs to compensate for a high humidity condition, their only option is to increase the area temperature. Needless to say, Air Temperature and Relative Humidity levels vary throughout any given day and have done so throughout the entire time period examined in this study. Average daily values for Air Temperature and Relative Humidity along with estimates for Water Vapor Pressure and Dew Point Temperature were tabulated and are plotted in [Figure 1](#).

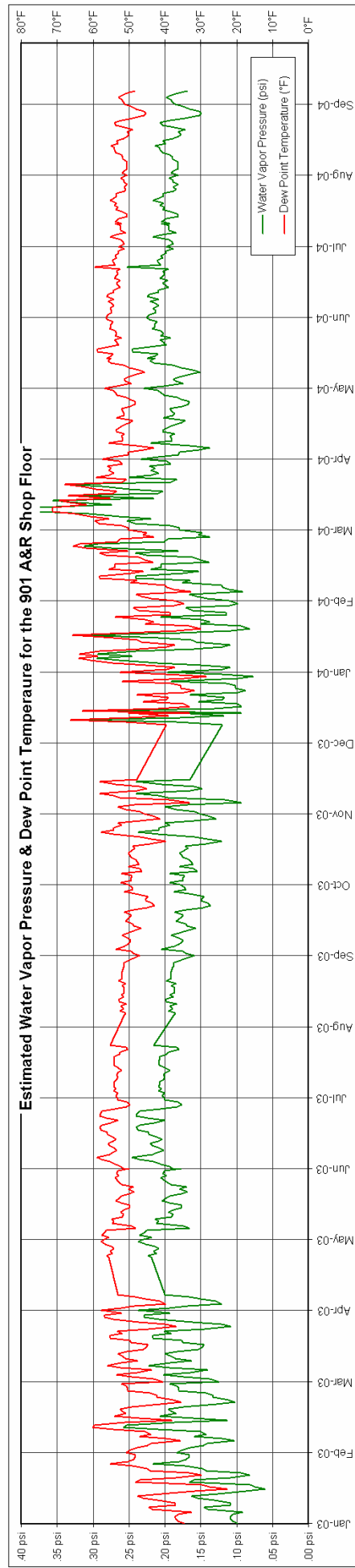
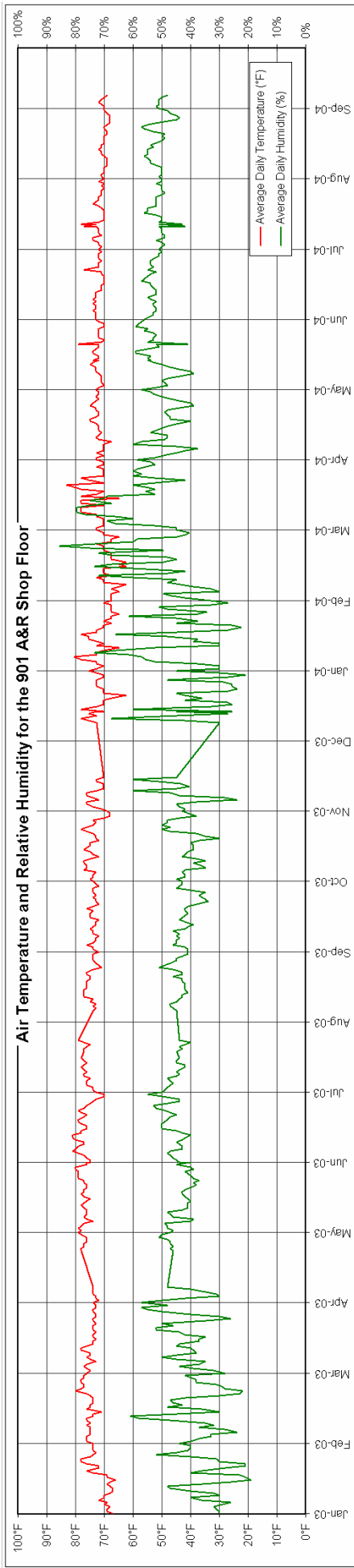


Figure 1. Plots of Air Temperature, Relative Humidity, Water Vapor Pressure and Dew Point for the South A&R Floor

### Analysis (continued)

The Magnus-Tetens model has been employed occasionally in the literature to derived values for saturated water vapor pressure <sup>(2)</sup>. This model defines the Saturated Waper Vapor Pressure,  $P_{ws}$ , as a function only of the ambient temperature and can be expressed by

$$P_{ws} = 0.6105 \exp\left(\frac{17.27T}{(237.7 + T)}\right)$$

where  $T$  is given in °C. These results can be converted to units of psi when multiplied by 0.145 psi/kPa.

Now it is well documented that the Actual Water Vapor Pressure,  $P_w$ , can be written as the product the Saturated Water Vapor Pressure and the Relative Humidity,  $H$  ...

$$P_w = H P_{ws} \quad (1)$$

When air is saturated, the Relative Humidity is equal to 100%, and the temperature is equal to the Dew Point Temperature,  $T_D$ , from which...

$$T_D = \frac{237.7 \left( \ln(H) + \frac{17.27T}{(237.7 + T)} \right)}{17.27 - \left( \ln(H) + \frac{17.27T}{(237.7 + T)} \right)} \quad (2)$$

Even though there has been minor concern expressed by other researchers regarding the level of uncertainty expressed by these relationships, we have employed Eq (1) and (2) to generate represenative estimates for the actual Water Vapor Pressure and Dew Point Temperatures used in this study.

Specific process dates for all 901 Blade Assemblies, Spars and Spar Assemblies manufactured in the A&R shop were tabulated for the period January 1, 2003 through September 13, 2004. Additionally, all parts with void-type defects and associated QMS documents were identified and confirmed so that 'good' and 'bad' parts could be plotted together on a timeline with Air Temperature and Relative Humidity. This is done in [Figure 2](#) for the 901 Blade Assembly, Molded Spar (assembly) and Spar Assembly. However, these plots do not indicate any significant revelations and are shown here primarily for illustrative purposes.

Estimated Water Vapor Pressure values on the specific process dates for defective parts are plotted in in [Figure 3](#). Again, these graphs do not provide a great deal of conclusive information, but they do illustrate the tendency for voids to occur on days when the local atmospheric water content in the south A&R shop was relatively high (at least for the Blade and Spar Assemblies).

Occurrence of Defect & Non-Defect Parts Relative to History of A&R Shop Floor Conditions

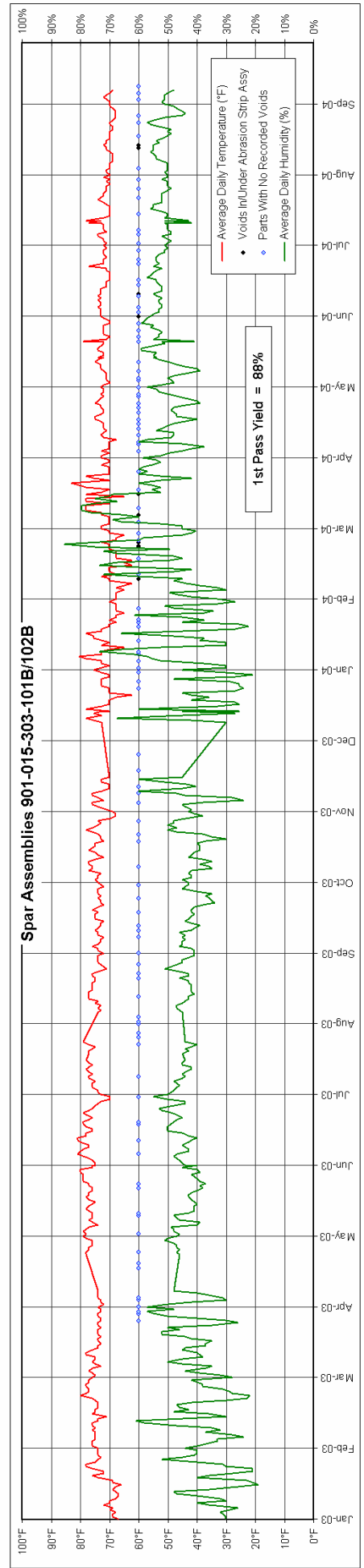
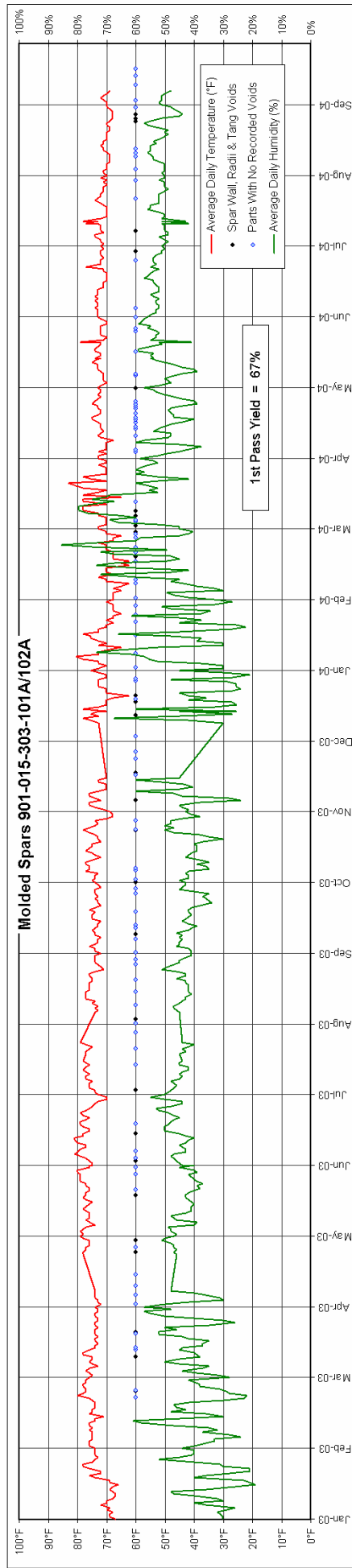
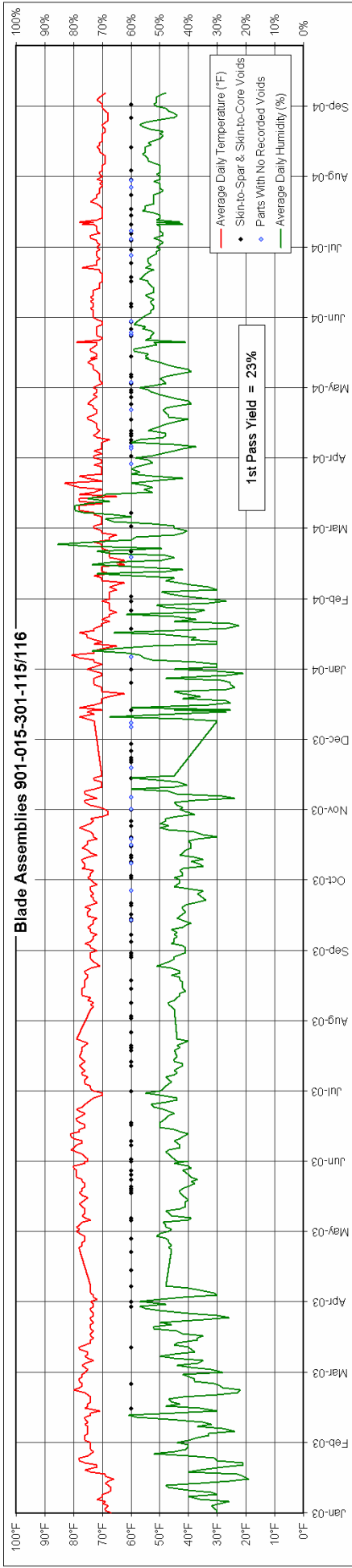


Figure 2. Plots of Shop Floor Air Temperature and Relative Humidity on Specific Manufacturing Days for 901 Blade Assemblies, Molded Spars and Spar Assemblies

### Estimated Water Vapor Pressure values on Specific Process Dates

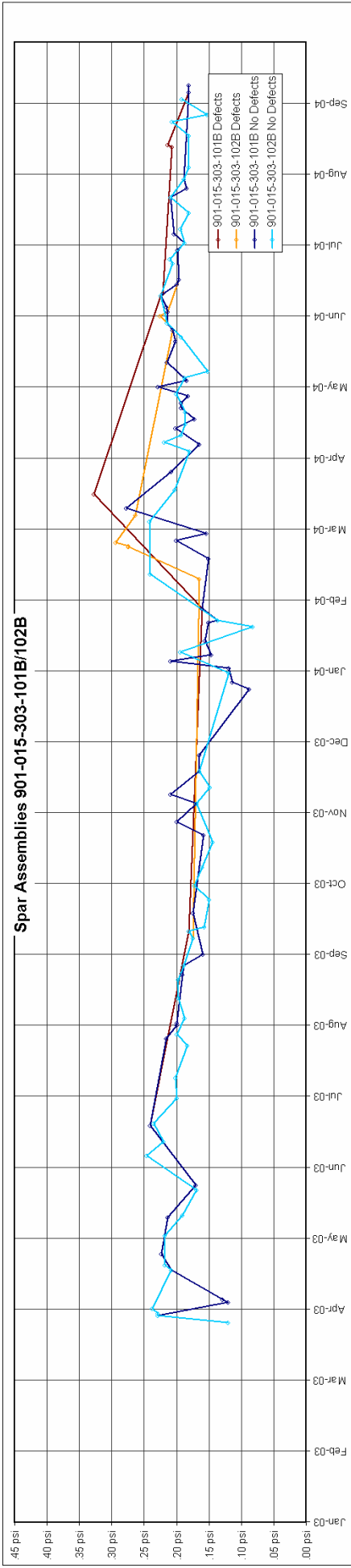
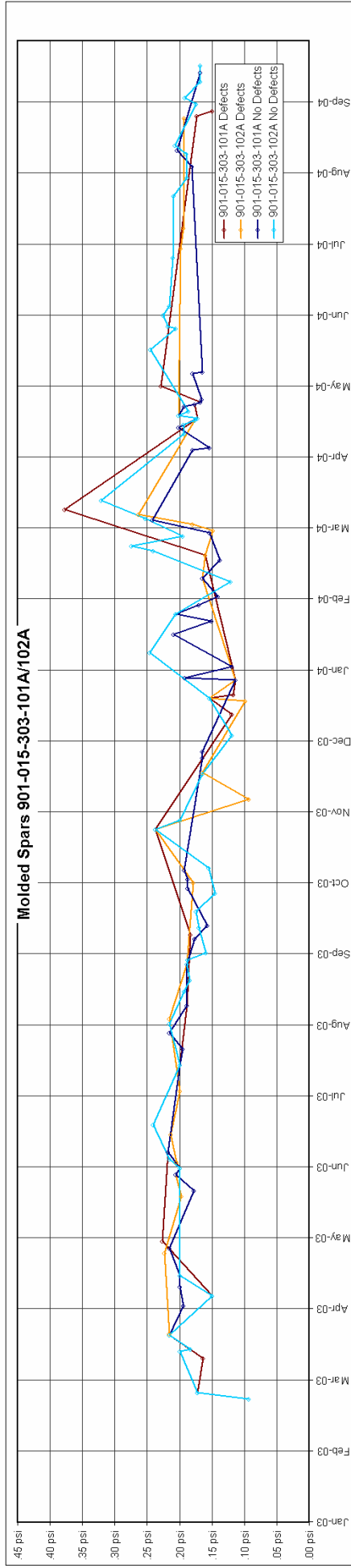
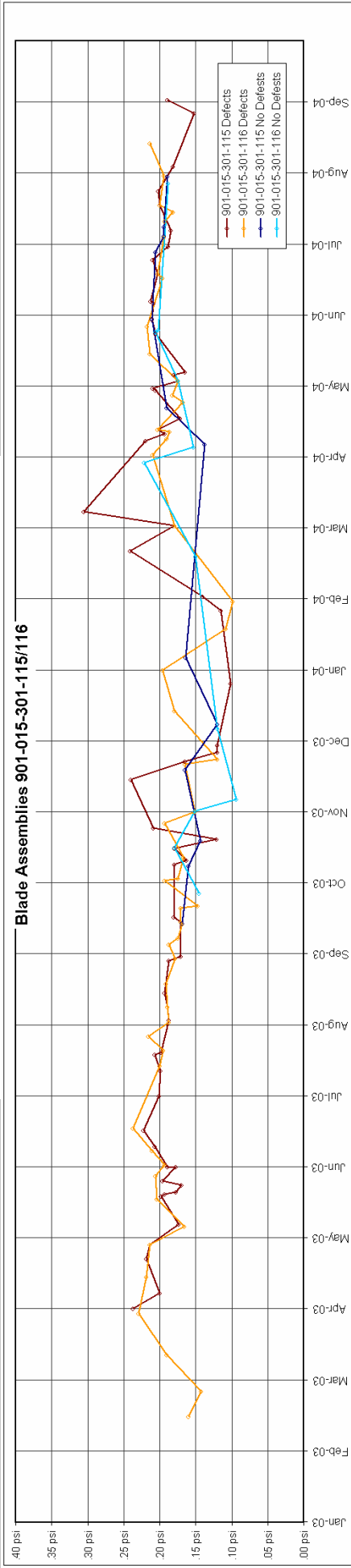


Figure 3. Plots of Estimated Water Vapor Pressure in the South A&R Shop on Specific Process Dates for 901 Blade Assemblies, Spars and Spar Assemblies

### Analysis (continued)

Now the data was averaged on a month by month basis to illustrate the behavior of Failure Rates on a more periodic-type basis. Here, Failure Rate is defined as the ratio of 'bad' parts (parts with 1 or more voids documented in the QMS system) to 'good' parts (those with no QMS documents for voids). It might be noted that the Failure Rate is equal to:  $1 - \text{First Pass Yield}$ . Monthly averages for Failure Rate, Air Temperature and Relative Humidity are given in *Figure 4* for Blade Assemblies, Spars and Spar Assemblies.

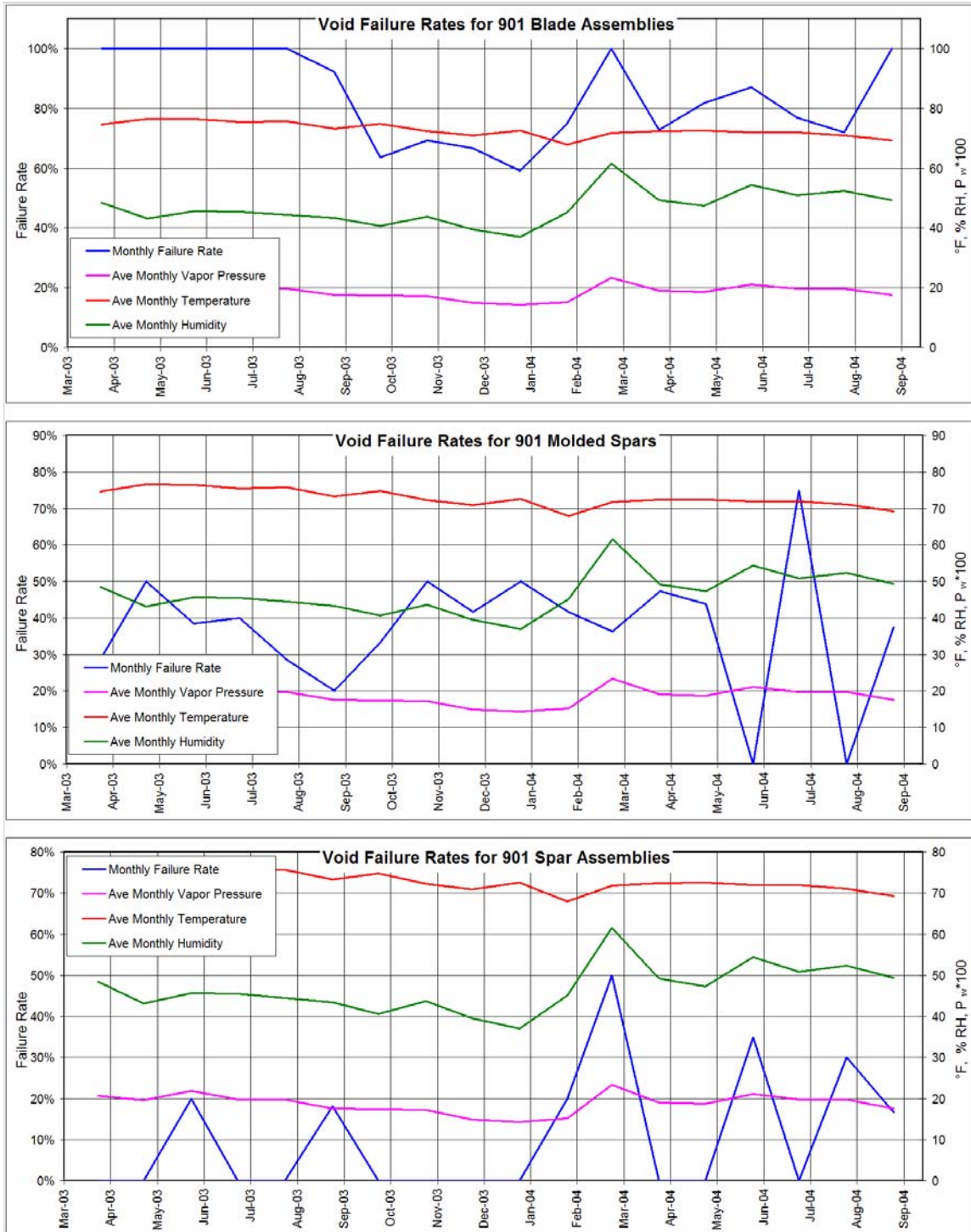


Figure 4. Plots showing contrast (or correlation) between monthly averages for Failure Rate, Air Temperature, Relative Humidity and Vapor Pressure for 901 Blade Assemblies, Spars and Spar Assemblies.





## Discussion

There are two possible scenarios (or failure mechanisms) recommended for further study when considering the effects of temperature and humidity on the formation of voids in 901 A&R components: (1) Direct correlations between hygroscopic properties of the constituent materials in Blade and Spar Assemblies relative to shop floor humidity levels, and (2) CTE (thermal expansion/contraction) compatibility between the various joining substrates and interfaces that make up the assemblies and associated tooling. Studies concerning CTE mismatch concepts may be explored in future efforts. In this paper, humidity-related hygroscopic effects are examined in conjunction with intrinsic chemical processes which may be responsible for the *generation of moisture* from within the constituent materials during assembly operations. However, it should be noted that resources were not available to acquire necessary chemical/physical analysis on specific materials currently used during shop floor processes to validate any suppositions provided here. Thus, these theories are only speculation.

Now the common factor between all Blade and Spar Assemblies is the use of the adhesive film AF-163-2 and its supported forms. A closer examination of this material is order. While the MSDS for 3M's AF-163-2 Scotch-Weld Structural Adhesive Film does not reveal the exact composition of the material and certainly eludes any of their closely guarded trade secrets, much can be inferred by the ingredients that are listed:

(1) dialkyl amine / phenolic epoxy resins / polyhaloepoxy resin (TS) . . . . .	40 – 70%
(2) epoxy resins . . . . .	15 – 35%
(3) dicyandiamide . . . . .	3 – 7%
(4) non-volatile amide (trade secret – TS) . . . . .	0.5 – 1.5%
(5) 1,4-bis[(2,3-epoxypropoxy)methyl]cyclohexane . . . . .	0.5 – 1.5%
(6) N,N'-(methyl-1,3-phenylene)bis(N,N',-dimethylurea) . . . . .	0.5 – 1.5%

Component (1) contains the primary bonding agent which is believed to be an *epoxy-crosslinked phenolic resin*. It is postulated that this single component is directly related to the mechanism of adverse moisture absorption, as well as additional moisture generation due to advanced phenolic hydroxyl condensation reactions. The amine is a curing agent for the resin(s) and the polyhaloepoxy (probably a bromonated epoxy) is believed to greatly enhance fire retardancy. Components (2) are most likely typical epoxy resins based on bisphenol-A. Components (3) and (4) are latent curing agents and/or accelerators designed specifically for epoxy-modified phenolics to enhance their storage stability while promoting rapid cure at elevated temperatures. Components (5) and (6) are reactive solvents.

Information is not readily available concerning epoxy-phenolics, and their chemistry is generally not covered in polymer textbooks, but much can be surmized by considering the independent attributes of phenolics and epoxies. Generation of water molecules during heated cure of base-catalyzed phenolic resoles due to primary reactions between phenol, aldehyde and their in-situ descendants is well known and documented<sup>(3)</sup>. Acid-catalyzed phenolic novolacs often require amine crosslinking agents to form networks, but more recently, epoxy oligomers have been utilized as such in efforts to prevent moisture production during the final crosslink condensation reactions. However, condensation reactions between residual phenolic reactants and/or reactive contaminants may be more prevalent than expected. In addition, advanced condensation reactions between unreacted phenol hydroxyl groups is inevitable, regardless of the type of phenolic precursor used. Epoxy hydroxyl groups, while fewer in number, can only exacerbate the situation.

It goes without saying, that applications which are sensitive to the effects of moisture are negatively influenced by the use of manufacturing materials utilizing phenolic resin components. Owners of these type of production applications should anticipate the requirement for periodic raw material testing in order to check for latent moisture generation as well as retainment of absorbed atmospheric moisture. Moisture content analysis can be accomplished using simple resin solids tests, or more precisely, by Thermogravimetric Analysis (TGA), both of which are low cost, quick analytical tools common in most materials analysis laboratories. The Bell Materials (M&M) Testing Lab does not currently evaluate incoming AF-163 materials for moisture content.

The high concentrations of phenolic and bromonated epoxy resin in AF-163 is expected to provide a high level of fire retardancy for the formulation (compared to other typical combustible polyorganics). It is believed that the vendor (3M) prepares the AF-163 resin mixture by blending a phenolic novolac prepolymer resin of predetermined molecular weight with a difunctional bisphenol-A based epoxy (a diepoxy) resin of predetermined molecular weight (it is also believed that the vendor produces all required prepolymers from scratch). After blending of all the other components, the product is a highly viscous solid film material that is below its cured Glass Transition Temperature ( $T_g$ ). When the proper temperature is reached during cure, the dicyanamide, nonvolatile amide and dialkyl amine act together to provide the initiation and acceleration necessary for completion of the crosslinking process which joins the phenolic segments together through epoxy bridges in the harden (cured) state as illustrated in [Figure 6](#).

**Discussion** (continued)

Generation of water in phenolic systems from condensation reactions during cure is inevitable. Moisture levels in AF-163 adhesive are not currently monitored by Bell M&M.

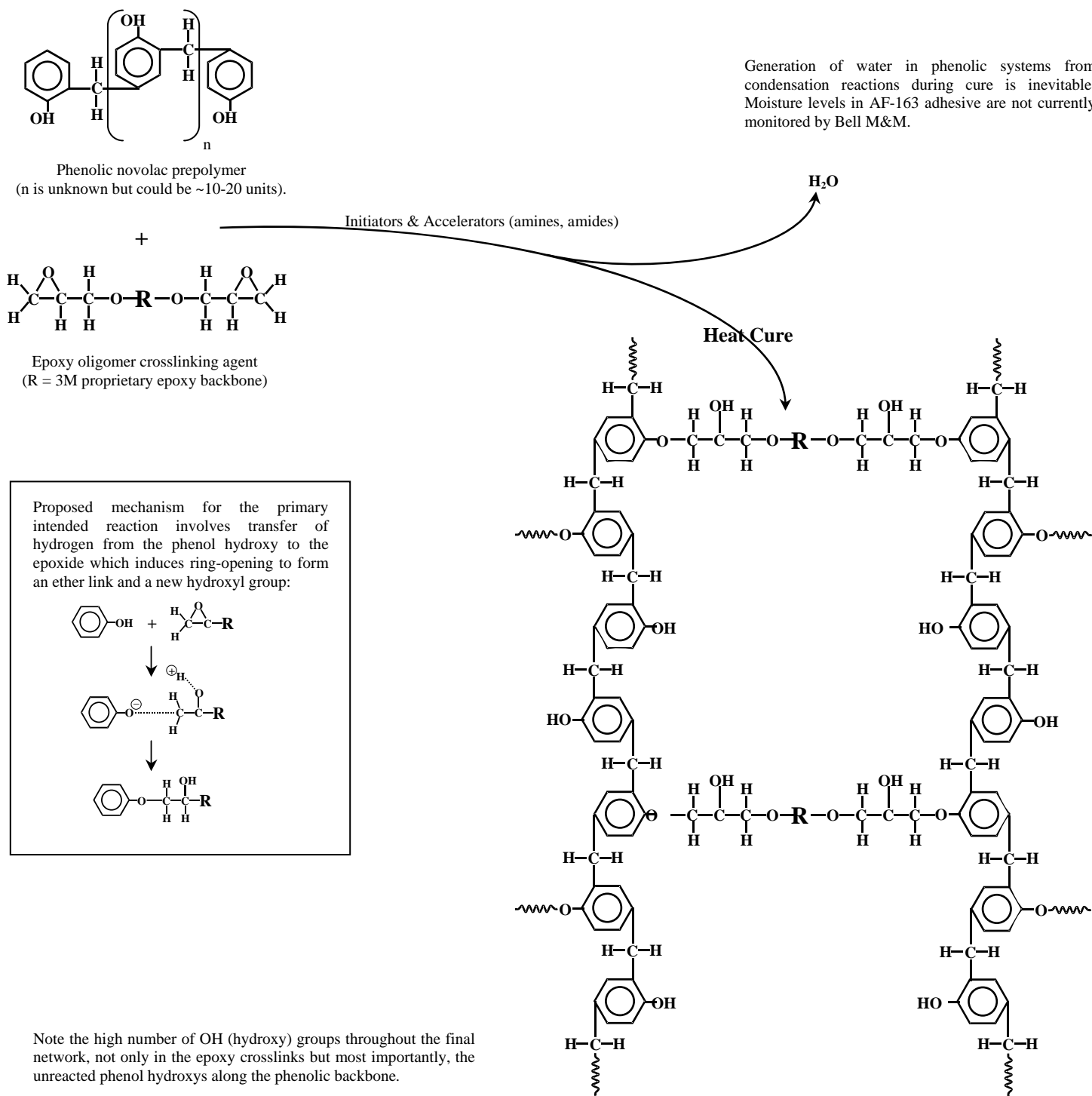
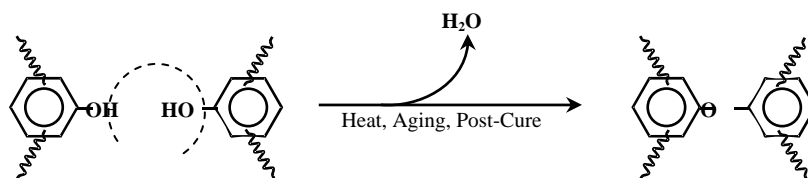


Figure 6. Structures, likely reactions and mechanisms for proposed phenolic novolac prepolymer and diepoxy oligomer which are blended together with amine/amide initiators and accelerators and then cured to form the final epoxy-crosslinked phenolic network.

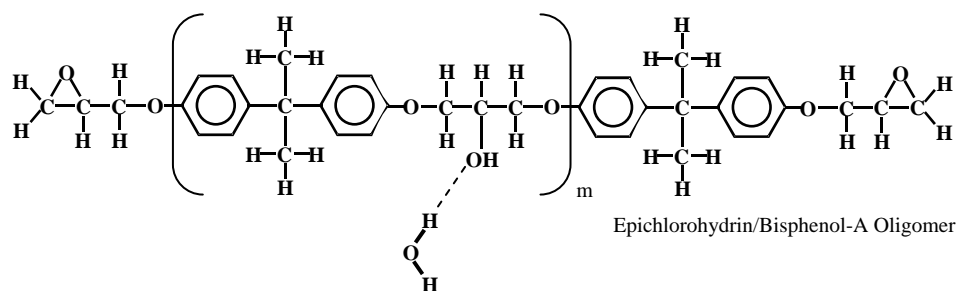
## Discussion (continued)

Residual condensation crosslink reactions are likely to occur with phenolic systems containing unreacted phenol hydroxyl (OH) groups over the lifetime of the resin, particularly during extended out-times and applications of heat:



Crosslinking reactions involving OH groups in the epoxy bridges with other OH groups in the system can also occur in the same manner. Indeed, the primary purpose of effective post-cures when applied to thermoset systems is to complete as many of the residual crosslinks as possible within the network since the net result is enhanced toughness and improved oxidation protection (not all crosslink reactions necessarily produce water). However, for networks containing phenolic segments, residual crosslinks will generate water which must be allowed to escape the system unimpeded without creating voids or stresses. In many cases, changes in OH concentration can be measured semi-quantitatively from Fourier Transform Infra-Red (FTIR) spectroscopy studies.

Now, hydrogen bonding occurs primarily between two groups, each containing an electronegative oxygen atom, that share one of their hydrogen atoms. Water molecules will hydrogen bond with themselves, which accounts for its high boiling point and expansion during freezing. Most importantly, water molecules will hydrogen bond with OH (hydroxyl) groups inside polymer networks, including the OH groups in epoxies and phenolics as illustrated in [Figure 7](#)



Almost all epoxies contain at least a few hydroxyl groups which can form hydrogen links with absorbed water molecules.

Phenolics contain ample hydroxyl (OH) groups to participate in hydrogen bonding with absorbed water.

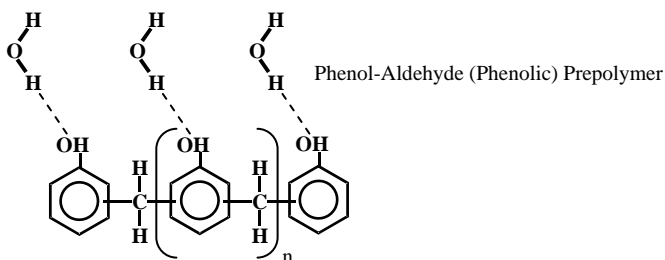


Figure 7. Illustration of hydrogen bonding (H-bonding) within the phenolic-epoxy blend showing likely bonding sites. Not shown are the additional H-bonding interactions that occur between absorbed water and the various nitrogen atoms present in the material due to the curing agents and accelerators.

Because of the abundance of OH groups in most thermoset systems, hydrogen bonding (H-bonding) is already a major factor in the quaternary structure and plays a prevalent role in the 'dry' glass transition temperature ( $T_g$ ) of the material. However, absorption of water in most polymer systems causes a marked decrease in  $T_g$ . Changes in the cured  $T_g$  have been measured and noted in 3M's product bulletin for AF 163-2 adhesive film after water saturation<sup>(4)</sup>. While their results are quite limited, Table I of that bulletin gives a dry  $T_g$  of 226°F and a wet  $T_g$  of 180°F for cured AF 163-2 (after 14 days in 160°F water). It is surmised that decreases in  $T_g$  for the AF-163 resin system due to absorbed water are a result of hydrogen-bound water molecules, whose effect is to disrupt the quaternary network, replacing structural H-bonding links with H-bonded water molecules. The incorporated water imparts a plasticizing (softening) effect accompanied by swelling of the material which further enhances the water absorption process.

**Discussion** (continued)

A good example illustrating changes in  $T_g$  relative to moisture content is given for Derakane vinyl ester resin in Figure 8<sup>(5)</sup>. Epoxies and phenolic-epoxies are expected to demonstrate similar behavior.

Moisture diffusion into *cured* polymer networks is dependent upon the polymer-water affinity (H-bonding sites) and the availability of molecular-sized holes which is directly related to the crosslink density. In the *uncured* state however, there are no crosslinks and water molecules are allowed to go into 'solution' with the resin, attaching to any available H-bonding sites along the way. Traditional models have centered around Fick's classical law of diffusion to explain moisture transport into cured polymer systems which defines the diffusion coefficient in terms of exposure time. However, these approaches are all based on cured, hardened polymer systems in which the polymer phase has no mobility. There are many publications throughout the literature applying Fickian diffusion concepts to various polymer systems<sup>(6) (7)</sup>, and there are a few applications relevant to epoxy matrix systems<sup>(8)</sup>. In brief, the one dimensional Fick's law of diffusion (in a solid medium) is often given as...

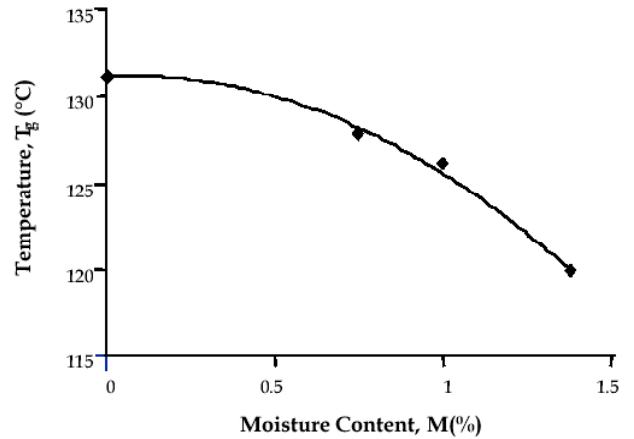


Figure 8. Decrease in  $T_g$  due to absorbed moisture for a vinyl ester resin – Most thermosets containing polar groups are expected to react similarly.

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2}$$

where  $D_x$  is the diffusion coefficient for water, and  $c$  is the water concentration. After converting to weight units, rearranging and simplifying,  $D_x$  can be written as a function of the saturation moisture content...

$$D_x = \left(\frac{\pi}{16}\right) \left(\frac{S}{M_{sat}}\right)$$

where  $S$  is the initial slope of moisture weight increase over exposure time. For true Fickian behavior, the process of moisture absorption occurs over time until the saturation plateau is reached as illustrated in Figure 9.

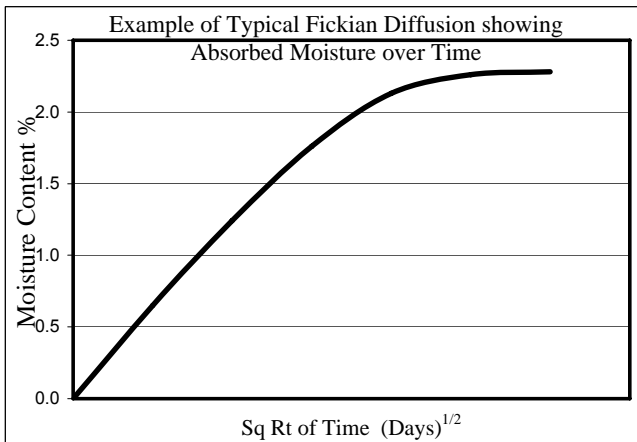


Figure 9. True Fickian diffusion follows a well defined curve of absorption and should always level out at some maximum plateau of moisture content.

The saturation moisture content is typically denoted as a power series of the Relative Humidity<sup>(9)</sup>...

$$M_{sat} = aH^b$$

where  $a$  and  $b$  are constants to be determined.

However, let us re-consider the implications from Figure 5 in the Analysis section and presume that the void failure rate is proportional to the moisture content. For our particular situation, curve fits have already been generated. For example, the Saturated Moisture Content (or Failure Rate) for both the Blade and Spar Assemblies can be given by exponentials...

$$M_{sat} = Ae^{kH} \propto F$$

where  $A$  and  $k$  are constants characteristic to the particular Assemblies, and the moisture content  $M_{sat}$  must be determined by gravimetric methods. All in all, there is much disagreement throughout the industry over which conditions are Fickian and which are non-Fickian. Some of these concepts include limitations based on resin stoichiometry (epoxy content vs. amine content), diluted polymer systems vs. concentrated ones, diffusion temperature (relative to  $T_g$ ), and crosslink density which is not relevant to

## Discussion (continued)

uncured resins. It seems that straight versions of Fick's law do not adequately define the process of moisture absorption/diffusion into *uncured* polymer systems, particularly when considering temperatures below their  $T_g$ .

Modified versions of Fick's law have been developed and appear throughout the literature based on a variety of properties and presumptions<sup>(9) (10)</sup>. Consider for instance, the free volume concept in which the spaces within the polymeric mass (between the polymer chains) provide paths for diffusion to occur. In this concept, the free volume of the polymer represents 'holes' or porosity in which water molecules can diffuse through. After all of the available H-bonding sites have been saturated (over an initial absorption period), this process may become significant as a mechanism for continual diffusion of water molecules into and out of the material prior to saturation.

Several models have been developed which make use of hydrodynamic (frictional) interactions during diffusion processes. These models also make use of the fact that the diffusion coefficient is heavily dependent on the concentrations of polymer and absorbed moisture. The frictional force exerted by the polymer on diffusing water molecules would determine the rate at which they pass through the material. This concept was first expressed by Fujita in the work of Crank & Park<sup>(11)</sup>. With this approach, the frictional force can be written as a function of the polymer and water volume fractions...

$$F_f = \frac{RT}{D_0} \exp\left(\frac{A}{Bx_w + x_p}\right)$$

where  $R$ ,  $T$  and  $D_0$  are the universal gas constant (8.3144 J/mol / K), the absolute temperature and self-diffusivity of water in 100% water; and  $A$ ,  $B$ ,  $x_w$  and  $x_p$  are the ratio of water volume to free polymer volume, the ratio of free water volume to free polymer volume, and the volume fractions of water and polymer respectively. Values of  $D_0$  for water at room temperature ( $\sim 25^\circ\text{C}$ ) have been published to be around...  $\sim 2 \times 10^{-9} \text{ m}^2 / \text{sec}$ .

Now Stokes-Einstein equations lead to an expression for the diffusion in terms of the frictional force<sup>(12)</sup>...

$$D_x = \frac{k_B T}{6\pi r_h \eta} = \frac{RT}{F_f} = D_0 \exp\left(\frac{-A}{Bx_w + x_p}\right)$$

where Boltzman's constant and its relation to the hydrodynamic radius for water molecules and system viscosity are shown for illustrative purposes. Since the free volume of water is negligible,  $B \approx 0$ , and...

$$D_x = D_0 e^{\frac{x_p}{A}}$$

However, the free volume of the polymer phase is completely unknown, and additional analytical tests would be required to estimate this quantity.

In an almost identical similar approach, Cukier developed a model which describes the diffusion process as hard spheres in a concentrated polymer solution, which are again, subjected to frictional interactions<sup>(13)</sup>...

$$D = D_0 \exp(-kr_h) \quad (3)$$

where  $k$  is the frictional or screening coefficient and  $r_h$  is the hydrodynamic radius of the diffusing sphere. For water molecules, it can easily be confirmed<sup>(14)</sup> that  $r_h \approx 1.45 \times 10^{-10} \text{ m}$ . The model also provides an expression for the screening coefficient when *coil-like* polymers are involved...

$$k^2 = \frac{F_f n_a}{\eta} = 6\pi n_a a \quad (4)$$

where  $n_a$  is the monomer number density and  $a$  is the monomer radius. For the present study, these parameters can only be surmised. In the case of AF-163, which is primarily a mixture of phenolic resin and high Molecular Weight (MW) epoxies, the MSDS s.g. is given as 1.53.

### Discussion (continued)

The monomer is not well defined in this situation since the direct ancestors to the network are actually pre-manufactured oligomers and prepolymers. However for the sake of discussion; lets presume the 'monomer' has a MW of ~ 107, corresponding to (approximately) a phenol group and associated methylene link, from which...

$$n_a \approx 1.622 \times 10^{23} \text{ monomers} / 107\text{g} \times 1.53 \text{ g/cm}^3 \times 10^6 \text{ cm}^3 / \text{m}^3 = 2.3 \times 10^{27} \text{ monomers} / \text{m}^3$$

Taking the average monomer radius to be equivalent to about six water molecules, we also have...

$$a \approx 6r = 6 \times 1.45 \times 10^{-10} \text{ m} = 8.7 \times 10^{-10} \text{ m}$$

And using Eq(3) and Eq(4), the diffusion coefficient for water in AF-163-2 resin can be estimated...

$$D_{AF-163}^{water} \approx 8.4 \times 10^{-10} \text{ m}^2 / \text{sec}$$

which is lower than that for water in water as one might expect. Recall that water diffusion is not only affected by polar and electronegative groups within the material, which can act as attenuation sites for H-bonding and dipole-dipole interactions, but the degree, size and nature of the permeability or microporosity throughout the polymer must favor the diffusion process. Some reports<sup>(11) (14)</sup> have given values in the  $10^{-11}$  to  $10^{-12}$  range for water diffusion through vinyl and polyester resins. These materials are expected to contain high levels of OH groups and acyl groups (=O), as well as ether links (-O-), polyhalogenated segments and possibly carboxylic groups (COOH).

Finally, the diffusion coefficient has been defined, throughout textbooks and the literature, to have a strong temperature dependence and is often given in its famous Arrhenius form...

$$D = D_0 \exp\left(\frac{-E_A}{RT}\right)$$

where  $E_A$  is the activation energy for diffusion from which...

$$\ln D = \ln D_0 - \frac{E_A}{RT} \quad \text{or} \quad E_A = RT \ln\left(\frac{D_0}{D}\right)$$

which gives a room temperature activation energy for water diffusion in AF-163 of...

$$E_A \approx 2.15 \times 10^3 \text{ J / mol}$$

No discernible values regarding  $E_A$  for water diffusion in epoxy systems at room temperature were available from literature sources, the internet or textbooks (much less for epoxy-crosslinked phenolics).

## Conclusions

While the technical discussion may provide some insight on possible scenarios relevant to void formation in AF-163 polymeric adhesive film, it really only serves as a starting point to characterize these particular types of defects. To summarize this quick study, let us start with the initial directive:

Variations in shop floor humidity were suspected by local engineers and managers to have a direct effect on the formation of voids in V-22 Blade and Spar Assemblies and possibly Molded Spar assemblies. The initial request was to evaluate this effect by starting with historical shop floor (south shop area) temperature-humidity charts over the past year or two, or as far back as possible. Data was tabulated and plots were generated for all available temperature-humidity charts which went back to around the first of 2003. South shop floor water vapor pressure and dew point estimations were explored regarding their relevance to shop floor atmospheric conditions. Distinctive correlations were inferred from the analysis indicating likely connections between average monthly humidity levels and void failure rates in 901 Blade and Spar Assemblies. The correlations also indicated that defect voids along AF-163-bonded interfaces in the Spar Assemblies might be heavily influenced by the shop floor humidity while AF-163-bonded interfaces in the Blade Assemblies could have other factors affecting the baseline void failure rate (such as tooling mismatch).

While there was no mandate or support budget, certain aspects of AF-163 adhesive were explored in a technical discussion intended to provide some insight into possible mechanisms regarding its interaction with atmospheric (shop floor) moisture/humidity. A more extensive project was initially planned to characterize the assemblies' component materials relative to thermal expansion/contraction (CTE) compatibility during shop processing *including* a more in-depth analysis of their respective hygroscopic properties. These projects are now on hold indefinitely. However, this study does permit some interesting conclusions to be drawn:

The phenolic regions of epoxy-phenolic resin systems (namely, AF-163), while adding many desired properties, greatly enhance the material's affinity to attract and retain atmospheric moisture. This is due to significantly increased levels of polar atoms and electronegative side groups, particularly hydroxyl groups that are provided by an abundance of phenol rings which make up the phenolic backbone of this material. Also, it is fundamental chemistry that both resole and novolac phenolic resins are formed by condensation reactions between phenol and formaldehyde in which each reaction (each link in the resulting polymer chain) corresponds to the generation of a water molecule. Any residual reactants present in the final film material will eventually result in intrinsic moisture generation (remnants of phenol in the case of novolacs). Furthermore, it is postulated that there is a high possibility for advanced crosslinking reactions to occur between unreacted OH groups subsequently or downline.

Due to the relatively high hygroscopic properties of AF-163 adhesive film, it is believed that absorption of moisture occurs continuously while the material is in use and/or exposed to the shop environment, and that the moisture content is directly related to the formation of voids. In essence, this theory supports the original suspicions related to the effects of humidity on the void failure rate. Once these water molecules are absorbed, they attempt to diffuse through the material until they become bound to electronegative side groups via hydrogen bonding (and possibly through dipole-dipole binding with polar groups as well). This process occurs, at least for an initiation period, until all the available reactive groups are consumed. It is unlikely the material ever comes near the saturation limit due to the relatively low humidity limits of the work area. Hydrogen bound water molecules are temporarily 'locked' in the structure until sufficient heat is absorbed to overcome the H-bond activation energy, which most likely occurs during the final temperature up-ramp of the autoclave cure. When released, water molecules will begin to coalesce due to dipole-dipole interactions and then subsequently volatilize, leaving the system and voids in their place.

## Recommendations

In their product data sheet, "3M Scotch-Weld Structural Adhesive Film AF 163-2", 3M has stated the weight loss for AF-163 to be less than 1% upon cure (determined by ASTM resin solids testing). However, the test is performed under tightly controlled conditions which essentially eliminate absorption of atmospheric moisture throughout the test. So this value would supposedly represent (primarily) condensation water product. While there is no concrete reason to doubt this report, there is also no historical evidence that Bell M&M has ever evaluated the material for this property, and it needs to be checked. It is recommended that incoming tests be considered regarding moisture content analysis for AF-163 material in order to validate vendor claimed volatile levels, to monitor absorbed moisture levels and lot-to-lot variations. It should be noted that, regardless of how well a resin manufacturer may control their processes, any resin containing phenolic components is prone to: (1) atmospheric moisture absorption due to strong hygroscopic properties (unfortunately, this applies in varying degrees to most epoxies, vinyl esters, cyanate esters and polyesters as well), and (2) internal moisture generation resulting from residual condensation reactions and/or latent crosslinking reactions. In addition, further studies are recommended to validate (or refute) the suppositions presented in this paper with a higher level of analytical support than was available for this study.

Consideration of alternative adhesives may or may not be a viable recommendation. It should be noted that incorporation of substantial phenolic portions into bonding material formulations, greatly enhances *fire retardancy* and provides the physical properties necessary for producing hot melt type film adhesives which are solid, pliable, handible, easy to apply, and make excellent bonding agents which can be quickly cured by heat application. Studies into other film adhesive compositions or even paste forms might be considered.

Tooling mismatches for the 901 Blade Assemblies are suspected to be a major factor contributing to void formation along the Skin-To-Spar and Skin-To-Core interfaces. Personal observations and comments from operators have indicated this to be a significant concern of long standing. Tool-To-Skin gaps need to be better defined and a method needs to be developed to physically measure and monitor these gaps so that the end product is not based solely on unverifiable numbers generated in a Catia design years ago.

Surface roughness requirements for adequate application of AF-163 were not investigated in this study (due to time constraints). There seems to be a debate over shiny vs. dull... Perhaps a Gloss Meter should be employed to characterize this property (gloss meters are common to the paint and coatings industries). However, proper adhesion is also heavily dependent on the surface chemistry and the nature and level of contaminants present. Here, the primary culprits are compounds (and elements) that can affect the surface pH, ionic conductivity (salts), and insoluble oils. Oils (organic polymers or oligomers) should only be insoluble in polymer resins if they contain ionic contaminants, such as human oils which are laden with salts. Ionic remnants on contact surfaces can sometimes cause localized lowering of pH levels and/or electrostatic effects which could adversely affect the resin's wettability characteristics and possibly the interface resin composition (and even generate more water). Now particulate contaminants should only be a major concern if they are non-dispersible in the adhesive or coating media - again, particulates containing contaminants such as salts and low pH liquids are generally non-dispersible at the onset. In many cases, abrasives, dust or dirt contaminants that are *dry* and contaminate-free, should be fully dispersible in organic/polymeric media. Indeed, most polymer products throughout industry contain high loading levels of ceramic, oxide and sand-like particulates as vital components in their formulations (adhesives, sealants, paints, coatings, etc...).

AF-163 cure cycle optimization studies might help to refine the process and minimize the occurrence of defects. For example, consider shortening (or possibly eliminating) the 180°F hold since this material does not even come close to gelling until > 200°F (3M reports 103 minutes to gel at 200°F). It is designed to be rapidly heated up and cured (@ 250°-350°). This (fast) approach activates the latent initiators and accelerators and kicks the material off fairly quickly, as it should be. However, precautions should be taken to avoid thermal shock effects, and considerations must no doubt take into account the lagging heat conduction properties inherent with large masses of tooling and product material. Extended holds under ~200°, especially when under vacuum, can possibly move unreacted components around generating composition variations as the lower MW components (accelerators, initiators, monomers) migrate toward the vacuum port. The same is true for composite matrix resins (most resins in industry are solutions of monomers, dimers, trimers, oligomers, accelerators, activators, catalysts, inhibitors, surfactants, etc...). When cure cycles for resin-based systems include extended time periods at pre-gel temperatures *and* under full vacuum, composition gradients will inevitably develop as the components travel across the fiber surfaces at different speeds (ie.. lower MW components travel faster than higher MW ones). This 'chromatography' effect should be strongly considered when designing fiber/resin composite production methods. While vacuum bag fabrication techniques may be OK for laminated fiber/fabric composites, they might not be the best choice for the 901 Spar Assembly or Abrasion Strip where multiple layers of metals and organics are joined together in a single operation. A more in-depth study of thermal expansion effects for the various materials involved would be in line here.



## Recommendations (continued)

One of the long range goals of the current study was to explore the effects of thermal expansion/contraction or CTE mismatch between joining components. CTE mismatch is really more of a match/mismatch between the *moduli* of the adjoining materials since the stiffness of a mating component is the primary driver that limits its compatibility with a more flexible interface during temperature cycling. Thermal expansion/contraction effects do not impart stresses in a free standing (unrestrained) body. But when strongly bonded to a stiff adherent (ie.. one with a high modulus) whose CTE is also notably different, mechanical stresses are automatically built into the system upon cool-down. If the modulus of one adherent is high enough and if there is also a significant CTE difference, catastrophic disbonds, delams and fractures will be inherently imminent. Perhaps this topic will be pursued at a later date.

In closing, a few other notes and ideas are given here. Autoclave cycles for the molded Spars, Blade & Spar Assemblies were examined and it appears the QMS/MR system caught most of the cure cycle anomalies that resulted in defects subsequently detected by ultra-sonic or tap testing. While relatively few equipment failures and power outages occurred over the period (ie.. significant or complete losses of temperature and/or pressure), almost all failures/outages appeared to be directly related to voids (particularly in molded Spars). Variations in the  $\pm 10^\circ$  and  $\pm 10$ psi range had no apparent negative effects, as one would expect.

Following is a partial list of other concepts that were initially planned for the overall assignment:

There is evidence that adhesives in *paste form* may penetrate porous surfaces much better than do film adhesives. This might seem to be a messy, impractical approach, but it also might be worth looking into.

Adhesives should be applied to both mating surfaces, not just one, as currently done for all interfaces of the Blade and Spar Assemblies. There is plenty of science out there to support this application technique. Unfortunately, current NDE methods are not sensitive enough to determine which side of an interface joint a given void occurs.

Would plasma-etched surfaces produce better adherents than sandblasted ones? Perhaps, but plasma etch chambers would represent an enormous capital investment. Corona treatments and chemical etches might also be examined.

Studies of surface wettability and surface tension effects relevant to preparation methods for bonding operations would be invaluable and would be a interesting task to pursue. This project would also include investigations into various chemical adhesion promoters, coupling agents and surfactant technologies as well as physical processes and other mechanical surface prep techniques designed to enhance strong polymer-to-composite and polymer-to-metal bonds.

## Appendix

### NOMENCLATURE

Spar Caps and multiple glass fiber torque plies are molded together on an inflated bladder and cured in compression tooling on a heated press to form the Molded Spar. The Molded Spar is cured at 355°F for 120 minutes with a 390 minute hold at 220°F per MPI 4517-012-009N. The Heater Blanket is a thin, glass laminated circuit panel (glass/resin - copper clad – glass/resin) that is molded to shape (the blade leading edge) by an outside vendor and brought in house. The Abrasion Strip is a Titanium alloy article fabricated to shape (the blade leading edge) via superplastic forming by an outside vendor and brought in house. The outer Nose Cap is an almost pure nickel article that is electroformed from a nickel 'plating' solution by an outside vendor and brought in house. The Abrasion Strip Assembly is made by installing the Heater Blanket onto the apex of a Spar-shaped tool, followed by installation of the Abrasion Strip onto the apex of the Heater Blanket, and then installation of the Nose Cap onto the apex of the Abrasion Strip. The entire system is vacuum bagged, cured, de-bagged, separated from its tool and cleaned up (via sand/media blasting). The Abrasion Strip Assembly is cured at 315°F for 135 minutes with a 10 minute hold at 100°F per MPI 4458-012-15C. The Abrasion Strip Assembly is then installed onto the apex of its mating Spar (Molded), bagged and cured to make the Spar Assembly. The Abrasion Strip to Spar Assembly is cured at 285°F for 90 minutes with a 60 minute hold at 180°F per MPI 4458-012-020B. Throughout the assembly process and at every interface, the film adhesive AF-163 is used as the primary bonding agent at each interface, Nose Cap -to- Abrasion Strip, Abrasion Strip -to- Heater Blanket, and Heater Blanket -to- Spar interfaces. Generally, a double layer of the AF-163 adhesive is assembled by hand and then applied to the male face of each interface joint in the assemblies. A double layer consists of one ply of supported AF-163 and one ply of unsupported AF-163 – this is the composition of each bondline interface medium. Operators call this make-up a 'blanket'.

The primary sections of the Blade Assembly include the finished Spar Assembly as the leading edge component, HexPly epoxy-aramid honeycomb Core as the trailing or AFT body component, and pre-fabricated thin glass/epoxy Skin panels that cover the upper and lower Spar/Core surfaces (this is not all the components, just the main ones). In general, an AF-163 'blanket' is applied to all surfaces during the final phase of this assembly. But before AF-163 is used, the entire assembly is put together using VeriFilm (a removable surface proofing film), enclosed in a large tool fixture, consisting of upper and lower halves, which are tightened together to a specified torque. The next day, the assembly is dismantled and reassembled using AF-163 adhesive 'blankets' and additional AF-163 is applied to low areas as indicated by the VeriFilm. Final cure consists of baking the Blade Assembly, in its mold, at 275°F for 70 minutes with a 60 minute hold at 180°F per MPI 4458-012-17F.

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