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MOISTURE AND THERMAL DEGRADATION OF CYANATE-ESTER-BASED DIE ATTATCH MATERIAL

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ABSTRACT

Cyanate-ester-based thermo-setting die attach materials, commonly known as Low Temperature Die Attach (LTDA) are the newest innovation in Hermetic Die Attach Technology due to their improved manufacturability, high decomposition temperature and a moisture gettering effect. Although their dispensability and decomposition temperatures are well documented, little information is available on the effects of prolonged exposure to moisture and thermal conditions. A study was therefore conducted to investigate the behavior of LTDA under thermal and moisture conditioning.

Results of the experiment showed that the LTDA initially exhibit weight loss and subsequent weight gain after prolonged exposure. Incorporation of the moisture into the polymeric structure was verified by Infrared Spectroscopy. Die shear strength was also observed to decrease exponentially with exposure time. The time-to-failure equation (10 kilograms die shear strength) as a function of temperature and humidity was established to follow the model

$$t_f \cong (\%RH)^n \exp(E/kT), \; n < 0$$

Calculations for shop floor condition (25 C/55%RH) show that an exposure time in the order of 106 hours is required for the die shear strength to degrade to 10 kilograms for a 224x225 mil die.

1.0 INTRODUCTION

Die attach can be accomplished using one of several materials. A good die attach material must have attributes fitted to the desired functionality which often governed by mechanical, thermal, and electrical properties.' Sufficient adhesion is required to ensure that the die remain fixed in place when it is subjected to assembly processing or during actual device service. Thermally, it shall impart the least stress during expansion and effectively accommodate transfer of heat generated in the die to the package. Die attach in some devices, may provide electrical path to the device substrate or insulation as in the case of silver-filled glass die attach used in some cerdip hermetic packages.

The quality of die attach may not only be limited to the desired material functionality. Properties that should be inherent to the material are also in consideration of the die attach process. In hermetic packages, the high temperature eutectic and silver filled glass die attach process raise concern on mechanical, thermal, and diffusional stresses that greatly affect device performance, thereby prompting the use of a polymeric substitute processed at low temperatures. Good dispensability is certainly a process concern, which is necessary to minimize nonuniform die attach especially in large die. Nonuniform die attach can enhance die (or package) stresses (causing die cracks), thus becoming a reliability issue.

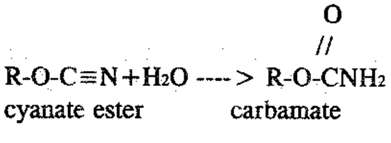
Another factor that affects not only die attach process but also device functioning is outgassing. Evolution of solvents in solvent-based die attach material in the succeeding steps e.g. curing, sealing, produce voids that are considered rejectable if it exceeds 15% of the die attach area. Voids are considered stress raisers and bring some degree of inhomogeneity in the die attach, altering some operational properties. In some hermetic packages, outgassing of dissolved moisture increases moisture content in the package headspace, consequently hasten a number of physio-chemical mechanisms that eventually lead to device failures. Thus, control of moisture in electronic packages is very important.

A new paste substitute processed at low temperature is in use since 1992. This material, internally known as LTDA-low temperature die attach is cyanate-ester based thermosetting polymer, claimed to have several advantages over conventional die attach materials. Cyanates, as compared to the conventional die attach, have high heat resistance and high adhesive strength at elevated temperatures. Most importantly, it exhibits a moisture "gettering" effect that can minimize moisture in the package headspace. These unique property of the cyanate ester paste, and the other factors that affect this property, is central to the study this paper intend to explore.

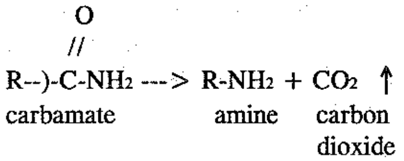
1.1 Moisture Uptake Mechanisms

Several works have dealt with the mechanism of moisture absorption of die attach materials, particularly cyanate ester paste. The moisture "gettering" of cyanate paste imply that a chemical reaction involving moisture has occurred. This reaction "traps" or "fixes" moisture in the polymeric structure, effectively preventing its evolution or outgassing during subsequent high temperature assembly process.

One work[1] stated the moisture uptake mechanism of the cyanate ester results in formation of intermediate carbamate, which consequently decomposes into an amine and carbon dioxide at temperature ≥ 200 °C. Thus, the reactions:



$$\underset{\text{cyanate ester}}{R\text{-}O\text{-}C{\equiv}N + H_2O} \;\text{----}{>}\; \underset{\text{carbamate}}{R\text{-}O\text{-}\overset{\overset{O}{//}}{C}NH_2} \qquad \text{(a)}$$

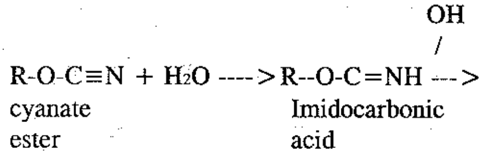


$$\underset{\text{carbamate}}{\mathrm{R\text{--})\text{-}\overset{\overset{O}{/\!/}}{C}\text{-}NH_2}} \longrightarrow \underset{\text{amine}}{\mathrm{R\text{-}NH_2}} + \underset{\text{carbon dioxide}}{\mathrm{CO_2}}\uparrow \qquad \text{(b)}$$

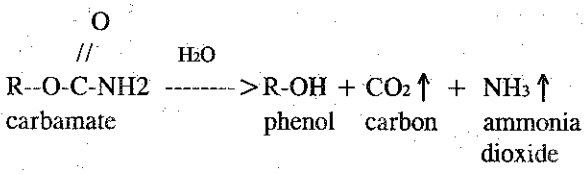
Overall reaction:

$$\mathrm{R\text{-}O\text{-}C{\equiv}N + H_2O \longrightarrow R\text{-}NH_2 + CO_2}\uparrow \qquad \text{(c)}$$

Tay S.T.[2] presented in his work another mechanism of moisture gettering of cyanate ester instead of the immediate formation of carbamate, an imidocarbonic acid intermediate is formed before the carbamate. The intermediate decomposes to form CO2 (same with the above), NH_3, and phenols. The reactions according to Tay S.T. as follows:



$$\underset{\text{cyanate ester}}{\mathrm{R\text{-}O\text{-}C{\equiv}N}} + \mathrm{H_2O} \longrightarrow \underset{\text{Imidocarbonic acid}}{\mathrm{R\text{--}O\text{-}\overset{\overset{OH}{/}}{C}{=}NH}} \longrightarrow \qquad \text{(d)}$$



$$\underset{\text{carbamate}}{\mathrm{R\text{--}O\text{-}\overset{\overset{O}{/\!/}}{C}\text{-}NH2}} \xrightarrow{\mathrm{H_2O}} \underset{\text{phenol}}{\mathrm{R\text{-}OH}} + \underset{\text{carbon dioxide}}{\mathrm{CO_2}}\uparrow + \underset{\text{ammonia}}{\mathrm{NH_3}}\uparrow \qquad \text{(e)}$$

Moisture as shown above indeed chemically react, decompose and become part of the die attach material. The chemical reaction is believed to be coupled with an adsorption process. The reaction sequence must be happening in a short time since the presence of the reaction products (phenols or amine) would present another material layer and require another step - the diffusion step. In the presence of product layer, the moisture molecule adsorbed in the outside surface has to take time to traverse or diffuse through the layer going to the cyanate active sites for reaction to occur. Thus, the diffusion-reaction-adsorption scheme will prevail most of the time. The establishment of which of these steps is the controlling step of the moisture "reaction" is yet to be established. However, one of the interests of the study is the bond disintegration and formation in the cyanate ester chemical structure brought by the moisture adsorption/ absorption. The investigation is made possible by subjecting to IR Spectroscopy the initial and moisture-exposed cyanate samples.

1.2 Rate of Moisture Uptake

The rate of moisture uptake at different temperatures is a relevant information as they relate to the exposure time during processing the paste in the manufacturing floor. Tantamount to this is the threshold of the moisture saturation of the paste. The rate of any chemical change can be calculated from the data collected showing change on the amount of material within a certain time interval of the chemical process. In the present case, the rate and saturation level of moisture uptake/ absorption can be deduced from the weight gain measurements after known elapsed time using a sensitive balance. The method, known as weight gain technique, has been applied and gave reliable results in several studies [3,4].

At present, the information on the rate and saturation levels at different temperature and humidity conditions are not available though they may have a high impact in the IC packaging that uses the new material. One objective of the study is to establish this information and relate them to the current manufacturing conditions.

1.3 Absorption Rate Factors: Temperature and Concentration

Rate of a certain physio-chemical process is usually affected by two factors - temperature conditions and material (substances or elements involved in the process) concentration. Materials in a relatively high concentrated state will react more aggressively (or vigorously), and at a faster rate. Taking the specific case of moisture-paste reaction, the limited paste may react at varying rate with the unlimited moisture amounts in the air, quantified by %RH.

Another factor that greatly affect the rate is temperature. If certain temperature-dependent process is directly or indirectly contributing to the failure of certain device, it is definite that temperature has something to do with how long the device will function, given presence of the materials and conditions necessary for the process to proceed. Seldom in many failure mechanisms the temperature does not have the key role, if not the main player, in its initiation, progress, or even acceleration, which can run up from ten to hundredfold. When the gradual progress, or even just the initiation, of failure mechanism pushed a certain parameter to the critical functional limit, the mechanism eventually manifest as catastrophic or functional failures in the device. The connection of this to the device functioning is that: at faster rate, device failure come in a short time; while the opposite is true if rate is slower, given that the other factors are kept unchanged.

The role of temperature on processes rate was studied by Arrhenius which is now incorporated in the equation, popularly known as Arrhenius Equation:

$$R = Ro \exp(-Ea/kT) \qquad \text{Eqn. (1)}$$

In the equation, R refers to the rate of certain physio-chemical process, Ro a constant, and k the Boltzman's constant, 8.6×10^{-5} eV/°K. The equation describes how the rate changes with temperature, T (in absolute scale, K: °C+ 273°) and activation energy, Ea (in electron volts, eV). The activation energy pertains to the energy a system should have surpassed for a process in that system to proceed spontaneously.

1.4 Moisture-related Failures

Moisture in the package presents many concerns. Presence of moisture at levels higher than tolerable can be rootcause of many failures in the die, and the package, both in plastic and hermetic packages alike. Moisture-related die failure can be chemical corrosion on the die metallization due to mobile ions which attack on Al, and moisture-induced delamination of thin film layers on the die. Electrolytic corrosion may also happen and be accelerated between biased metallization lines with the presence of moisture since it increases metallic ions mobility in the surface of insulators and conductors alike. Increase in metallic ions mobility enhance the conductivity of both the insulators and conductors. Thin film layer delamination can be due to H_2O attack (chemical dissolution) of P-doped oxide. High P levels in SiO_2 film layers and mechanical defects in the moisture barriers layers are the factors cited supporting the thin film delamination[5]. Hence, moisture is indeed a critical parameter concerning device sound functioning.

1.5 Rate and Time-to-failure Equations

The rate at which physio-chemical processes proceed, or some failure mechanism for that matter, is inversely proportional to the time to failure, t_f, of the device. This means a faster rate results in shorter device life due to a certain failure mechanism. Hence, basing on the Arrhenius equation:

$$t_f \cong 1/R \cong \exp(Ea/kT) \qquad \text{Eqn. (2)}$$

which transforms into a linear function of ln t_f vs 1/T,

$$\ln t_f = Ea/kT + C \text{ or } (Ea/k)(1/T) + C \qquad \text{Eqn. (3)}$$

At two different Temperatures, T_1 and T_2, with corresponding time to failures, t_{f1} and t_{f2}, the activation energy is determined from the slope of the plot ln t_f against 1/T.

The above approximation did not include the effect of relative humidity. A relationship between time-to-failure, surface temperature, and relative humidity was fitted to the data of D.S. Peck and O. Hallberg[6]. The expression has the form shown below:

$$t_f = A(\%RH)^n \exp(\Delta E/kT) \qquad \text{Eqn. (4)}$$

For corrosion related failure, the data of D.S. Peck gave a value of n and ΔE equal to -3 and 0.9, respectively, and with A the expression constant. The expression implies that time-to-failure due to corrosion is exponentially decreased to the third order by %RH. The temperature effect is that time-to-failure will be shorter with increasing temperature. One objective of the study is to determine the values for A, n and ΔE for the time-to-failure expression of die shear strength at different exposure conditions. The ΔE in this case is the combination of energies of activation of physio-chemical processes involved in the weakening of die attach adhesion strength. This processes, mostly associated with presence of moisture, are surface adsorption, reaction, and diffusion at interfaces.

1.6 Objectives of the Study

In summary, the objectives of the study are:

1) To determine the moisture saturation levels at different conditions of temperature and % relative humidity;
2) To develop applicable model equations; and
3) To determine the behavior of die shear strength degradation as a function of time at a given exposure environment.

2.0 EXPERIMENTAL

2.1 Materials and Equipment

2.1.1 Paste and Substrate

The material of primary concern in this study is the polymeric die attach paste, which is 80% silver-flakes in the matrix of a proprietary cyanate-ester-based resin.

Alloy 42 blank strips (5.0 x 3.0 cm) were chosen as the carrier substrate over the copper strips for the latter oxidizes quickly when exposed to severe environment. The oxidation of copper render the weight of moisture absorbed inaccurate, a situation minimized in Alloy 42.

2.1.2 Leadframe and Dice

In the investigation of the effect of moisture on die shear strength, the carrier leadframe used was Alloy 42, 350x350mils pad size, 28L PDIP. AD1846 inked dice (224x225mils) were selected and die-attached using the polymeric die attach paste, internally known as LTDA or low temperature die attach. Pad to die size ratio equals 40%.

2.1.3 Moisture Chambers

Humidity exposures was performed in Labstar Humidity Cabinet (LH-112), Trio-TECH HAST-1000X. The Humidity Cabinet performance ranges and constancy are as follows:

Temperature
Range: +10 to +85 °C Accuracy: +/-0.5 °C
Humidity
Range: 45% to 95% Accuracy: +/-3%RH (at 20 °C)

Dry-bulb and wet-bulb temperature indicating range of the cabinet is 0 to 99 °C.

The HAST 1000X is basically an autoclave for environmental testing, utilizing a two-chamber humidity test environments which solves the problem associated with producing both saturated and unsaturated steam in a single vessel. A computer-based controller is incorporated into the system which allows its operation by a pre-programmed algorithm performing variety of functions including data monitoring, graphic display, logging, power supply cycling, test times, etc. Temperature and humidity can be programmed with 0.1 °C and 0.1% resolutions, respectively. Operational ranges are as follows:

Temp.=50 to 179°C;
Pressure: 56 psig.;
Humidity = 50 to 100%RH
(-/+1.0% @ 100%RH, -/+2% @ 85%RH)

2.1.4 Electronic Balance

Measurements of moisture weight gained were done using an OHAUS electronic Balance model GA 110 with weighing range of 0 - 110 grams. Readability of the balance is up to the fourth decimal place, i.e. 0.0001 g. Precision (or standard deviation) and linearity is registered as -/+0.0001g and -/+0.0002g, respectively.

2.1.5 Die Shear Tester

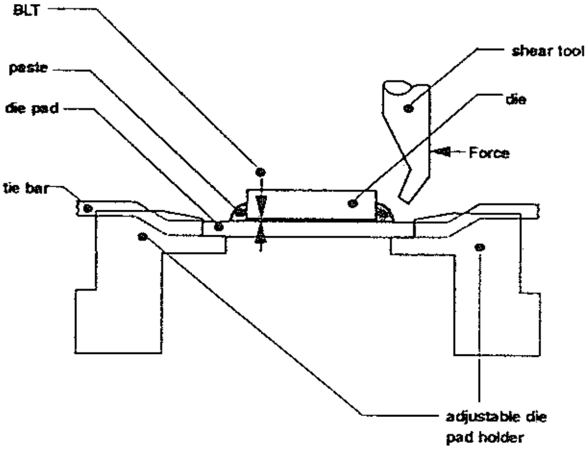


Figure 2.1 Schematic of the die shear tester

The die shear tester is composed of die pad assembly and a digital force gauge mounted on a platform. The die pad assembly is equipped with height adjustment and die alignment which allows centering the die with the shear tool. In the die assembly, an adjustable pad holder, which can handle several lead count PDIP leadframes, grip the pad in place against the shear tool force.

The digital force gauge (Chatillon Brand - DFIS) has a maximum force of 200 kg and 0.2 kg sensitivity. Figure 2.1 shows the schematic of the die shear testing.

2.1.6 IR Spectroscope and Sample Preparation

Two IR Instruments were used in this study. One was the Perkin Elmer Paragon 1000 FT-IR Spectrometer, equipped with IR spectrum software processor and is capable of the dispersive and ATR modes. In the ATR (attenuated total reflection) mode, the IR beam is allowed to reflect (or zigzag) within the sample in a special sample holder. This method ensures longer and more IR-sample interaction. The other brand was a Nicolet Series II Magna-IR System 750. The Nicolet system is also capable of the ATR mode and has a microscope attachment to provide nondestructive microanalysis with minimal sample preparation. Both systems were equipped with Windows-based software package, collecting and processing signal data. In the investigation, dispersive mode was widely used in which the ground sample is suspended in the KBr matrix. Sample preparation for the IR Spectroscopy consisted of pulverizing the hardened paste using an agate mortar and pestle, and mixing the sample with KBr. The ground sample was mixed with spectroscopic grade KBr (potassium bromide), weighing 20X the sample weight to maintain the 1:20 paste to KBr ratio. The mixture was pressed in a mold thin enough to become transparent to light. The thin film set in the mold, now already prepared unless it exhibited cracks, was immediately subjected to the IR dispersive scan.

2.2 Procedures

The conduct of the study followed the experimental flow-chart shown in Figure 2.2 The steps of each of the three major experimental segments - weight gain, die shear test of moisture-exposed samples, and the IR investigations - are reflected in the flowchart. Two steps are common in the three segments, that is the curing and moisture exposure steps. The following discussions provide the details of the experiments conducted.

2.2.1 Moisture Exposure and Weight Measurements

Three environments/preconditioning settings were considered for moisture exposure, namely: Humidity Cabinet 85 °C/85%RH, HAST 135°C/85%RH, and HAST 85°C/60%RH. Three samples, i.e. sample A,B,C, were prepared for one environment exposure, with each sample consisted of four A42 strips.

The A42 strips were ultrasonically cleaned to remove dirt and oil contamination. Each sample - consisted of four strips each - were weighed using a 0.0001g-sensitive electronic balance before dispense of paste. Paste was dispensed in X-pattern (0.5x0.5 cm in size). Curing was done on a multi-chamber Blue-M BI-16F-1 oven followed immediately. After curing, samples were weighed again, and the difference in weights before and after curing amounts to the paste dispensed for each sample. The weight of paste dispensed for each sample ranges from 2.0 to approximately 3.0 grams. The amount was made sufficient to ensure reliable weight gain measurements.

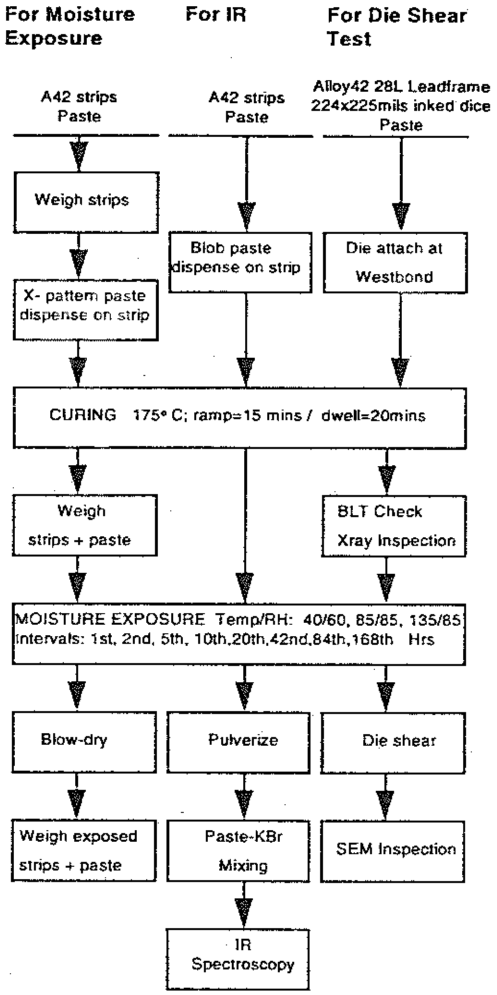


Figure 2.2 Experimental Flowchart

It has been reported[7] that cyanate paste cures (90% conversion) for 5 minutes at 175°C. Curing of cyanate-ester paste is maintained at 20 minutes in the assembly line to assure of complete curing.

The cured samples were exposed to moisture in the moisture chambers (HAST, Humidity Cabinet, PCT) for 168 hours. At the preset exposure intervals - 1st, 2nd, 5th, 10th, 20th, 42nd, 84th hour - the samples were retrieved from the chamber, allowed to cool for 10 minutes in a desiccator, and weighed in the electronic balance. Cumulative time of exposure did not include time the samples were outside the chambers during weighing. Exposure time commenced only after the weight gain samples were returned into the chambers.

IR investigation and die shear test have separate samples exposed to moisture together with the weight gain samples. There were eight (8) IR samples, and similarly eight 6-die strips for die shear, one each for different exposure time interval or retrieval from the moisture chamber.

2.2.2 Die Shear Strength Measurements

Shear measurements were done every after exposure interval on six (6) 1846 inked dice, attached to 28L A2 leadframe strip. The samples for die shear were prepared using manual West Bond in the die attach process. During shearing, the shear tool point touched the die side surface just above the paste fillet. Although shear strength is directly proportional to the area pasted, BLT measurement was done in the samples for the three environments to check consistency of paste dispense.

Xray inspection were also done to screen out void rejects. After die shear test, the dried and hardened paste residue in the strip were subjected to SEM inspection to compare morphology of exposed paste surface.

3.0 RESULTS AND DISCUSSION

3.1 Weight Gain from Moisture Absorption

3.1.1 Electronic Balance GR & R

The weight gained by the paste from the moisture exposure was a major output response. To ensure that the weight measurements were within the acceptable uncertainty and variability, the GR & R standard procedure[8] was conducted to check the electronic balance variation of measurements. The calculated R & R from the exercise was 3.0%, acceptable based on the AIAG* criteria which is 10% and below.

Preliminary Experiment in 85°C/85%RH

Preliminary run at 85°C/85%RH environment was conducted using four A42 strips with about 1.2 gram paste. One set of sample, consisting of four strips, was weighed every after retrieval from the humidity cabinet at time intervals mentioned before. The sample gave a negative weight gain in the first ten hours of exposure. The lowest was about 0.05% in the second hour. Positive weight gain was only encountered in the measurements done after the tenth hour. It was surmised that the variability of the balance was the one that triggered the negative reading change. To cope with the sensitivity of the balance, the paste was increased to 2 grams in each sample and at least three sets of samples for each run.

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* Automotive Industry Action Group

3.1.3 Weight Gain Behavior

Samples for the die shear test and IR spectroscopy were exposed to the 85°C/85%RH environment (in the humidity cabinet) together with the three sets of samples for the weight gain measurements. The results of the weight gain measurements indeed confirmed the negative weight change encountered in the preliminary experiment. Figure 3.1 shows the plot of percent weight gain versus logarithmic value of exposure time(in hours) for the 85/85 environment. Every point in the graph is averaged from %wt. gain of three samples in that time interval.

Figure 3.1 presents a negative weight change in the first three weight measurements-1st, 2nd, 5th hours. The lowest weight loss is estimated at -0.06%. Positive weight gain was encountered only after the 20-hour exposure and the succeeding exposures that followed. The maximum weight gain for 85/85 was recorded at 168th hour exposure. Additional measurement taken at 200th hour indicated moisture saturation since the fitted trendline started to level off in that time region.

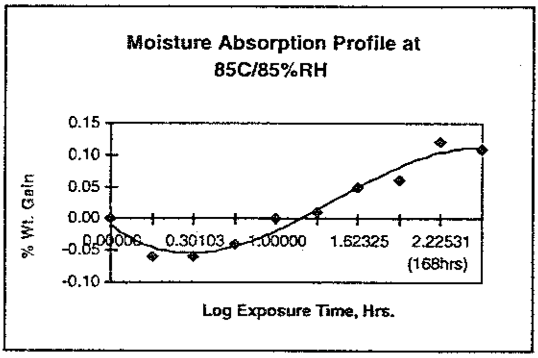


Figure 3.1 Moisture absorption profile for 85°C/85% RH environment.

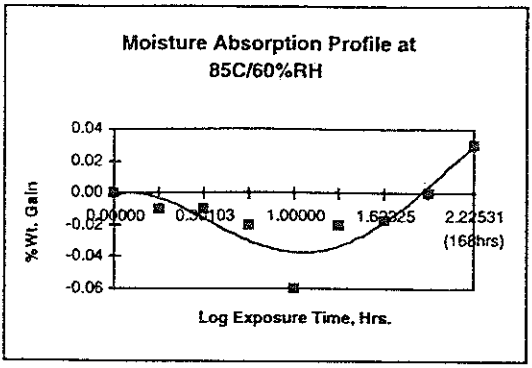


Figure 3.2 Moisture absorption profile for 85°C/60% RH environment.

Figure 3.2 is the moisture absorption data for the 85°C/60%RH environment. The figure also exhibited a behavior close to that encountered in the 85°C/85%RH. A negative weight change was also recorded and prevailed until the 42nd hour exposure. The lowest weight change was around same value as that in Figure 3.1, occurred at about 10th hour of exposure hour. This lowest weight change took longer as compared to 2nd hour in the previous profile. One difference that can be cited between the two profiles is its shape as the 168th hour is approached. The latter profile is rising as the 168th hour is approached, an indication the paste is still unsaturated. From the profiles, it can be deduced that the saturation level after 168th hour exposure was attained in 85/85 environment but not in 85/60 environment.

The initial weight loss observed above cannot be attributed to weight loss related to residual curing of the paste. Data[1] from TGA showed no significant weight loss during curing even at temperatures above 300 °C. Weight loss commences only at approximately 350 °C when the paste is undergoing chemical degradation.

Figure 3.3 is the moisture absorption profile after exposure in 135°C/85%RH environment. The profile does not show the negative weight change observed in the other two profiles. Instead of showing negative weight gain, the three samples registered positive weight gain values immediately after 1st hour measurement. Stabilization problem with the equipment precluded shorter exposure times which could have shown the initial weight loss phenomenon previously observed. The maximum weight gain was recorded at 5th hour exposure after which the weight gain begun to decrease at fast rate. The paste in this situation is surmised to have undergone some form of degradation which resulted into a rapid weight loss.

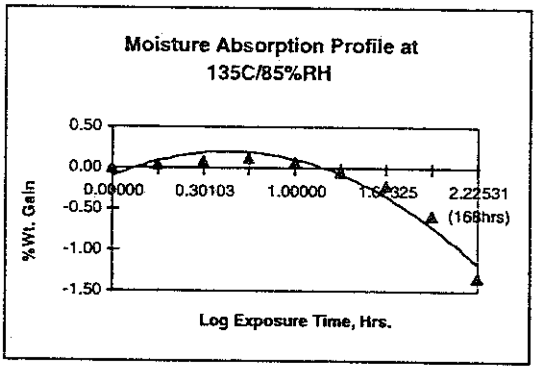


Figure 3.3 Moisture absorption profile for 135°C/85% RH environment.

The initial loss in weight of the paste during exposure may be explained by considering equation (c):

Gettering Reaction:

$$\text{R-O-C} \equiv \text{N} + \text{H}_2\text{0} \text{ ---> } \text{R-NH}_2 + \text{CO}_2 \qquad \text{(c)}$$

Notice that this reaction produces a negative weight gain since CO_2 is heavier than H_2O. Outgassing of CO_2 is deemed to occur on the outer surface of the paste during initial moisture exposure. As moisture penetrates into the interior of the paste, however, outgassing of CO_2 becomes more difficult, if not totally prevented by the polymeric structure of the paste (carbamate formation). This results in the positive weight gain of the paste with continued moisture exposure. This may also explain the previous observations that carbon dioxide is evolved at temperature in excess of 200°C. At these temperatures, structural changes in the polymer are possible to allow the decomposition of the carbamate and release CO_2.

3.2 Die Shear Degradation

3.2.1 Die Shear Strength Trendlines

The average shear strength of the die attach in every exposure interval is plotted against time as shown in Figures 3.4 and 3.5. Curves for a 85/85 and 135/85 environments shows abrupt degradation of die shear strength below 20 kgs before 25 hours exposure and approached zero at prolonged exposure. The die shear strength did not degrade much during exposure at 85/60 environment which registered at around 30 kgs. even after 168 hours exposure.

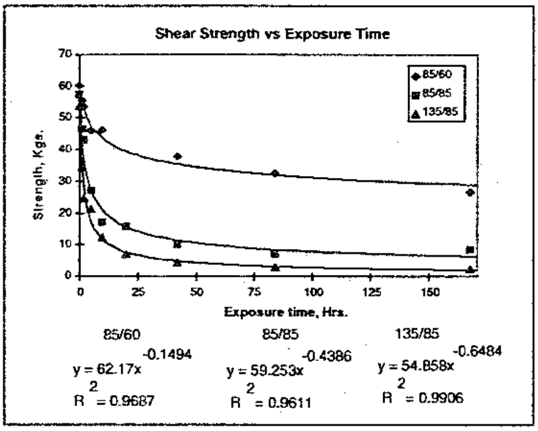


Figure 3.4 Die shear strength degradation at various exposure environments.

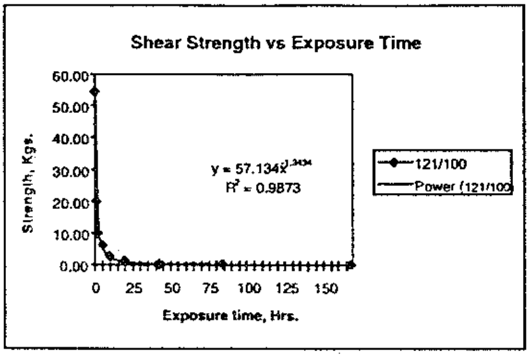


Figure 3.5 Die shear strength degradation at 121°C/100% RH environment.

Trendlines were fitted to the die shear strength data. The power functions have shown a good fit in the curves as indicated in correlation (R-squared) values for all the curves. R^2 values above 96% indicates a good fit of trendline function.

Additional die shear strength measurements were conducted in samples exposed to PCT condition (121 °C/100%RH). Figure 3.5 shows the behavior of die shear strength at this condition. After 5 hours exposure, shear strength registered below 5kgs. The effect of PCT condition is more severe than the 135/85 environment, as can be discerned in the negative power exponent of the variable x, referring to time in the trendline equation. The exponent in 121/100 trendline equation is -1.3434 while in 135/85 -0.6484.

The data of die shear strength testing indicated that the strength degrades to a critical level (< 5 kgs) only in conditions more severe than 85/85 environment. At 85/85 environment, strength was 8kgs. after 168th hour exposure. Mil Std 833 specifies that die which are larger than 64×10^{-4} in.^{2} shall withstand a force of 2.5 kg. The implication on the process is that the exposure of cured paste in the manufacturing floor will not induce any failures concerning the die attach strength and adhesion. This supports the findings of the previous work[9] concerning shear strength of LTDA.

Table 1. BLT measurement (in microns) of die shear samples.

Die	Batch 1	Batch 2	Batch 3
1	21.4	16.9	21.7
2	21.1	22.6	24.1
3	19.1	20.4	18.1
4	19.9	23.1	21.7
5	21.1	21.5	19.7
6	20.7	20.9	20.4
7	22.5	18.7	20.0
8	22.2	17.8	22.0
Average	21	20.24	20.96
Std. Dev.	1.12	2.24	1.8

3.2.2 Results of BLT Measurement and Xray Inspection

Eight dice from each batch of die shear samples were cross-sectioned in order to determine nominal bond-line thickness and its variability. BLT measurements are tabulated in Table I. Xray inspection conducted on the samples found no voids which exceed the 15% void failure criteria.

Based on Table I, BLT ranges from 16.9 to 24.1 microns. The measurement on the die shear strength done in this study assume that the variability brought by the deviation of 2.24 microns have a negligible effect on the shear strength. Further, fillet and coverage were made as uniform in all units as possible to lessen variable effects to the shear strength readings.

3.2.3 Die Shear failure Modes

Figure 3.6 to 3.7 were the common die shear failure encountered in the die shearing.

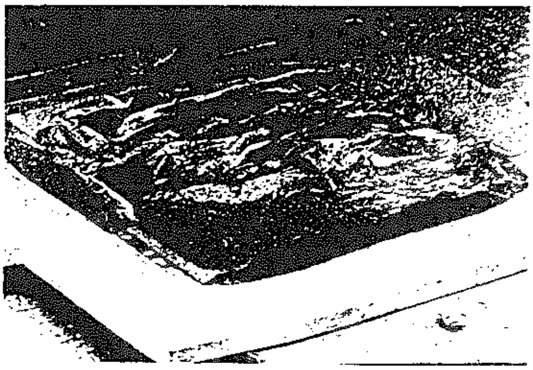


Figure 3.6 Die breakage during shear test.

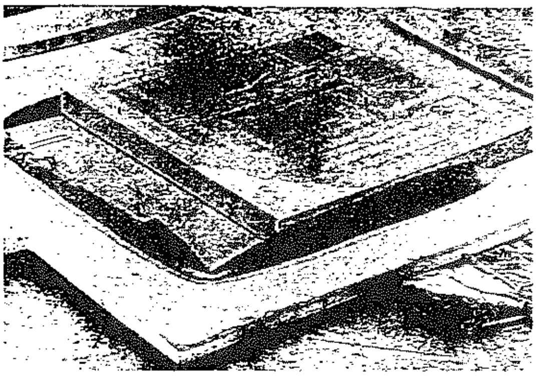


Figure 3.7 Failure of adhesion at the die-paste interface

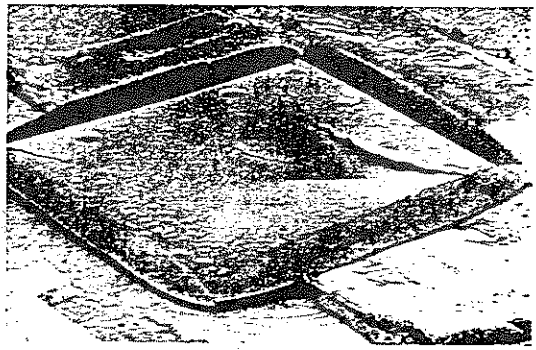


Figure 3.8 Failure of adhesion at the die-paste, paste-paddle interface

Figure 3.6 typifies the failure of die during shearing of unexposed samples. Strength for this type of shearing fell between 60 - 70 kgs. The strength readings was partly due to the breakage of the silicon die which indicated cohesion failure within the die. For a reliable die attach strength, failure in the die is the desired mode. Breakage of the die was indicative of a stronger adhesive. Readings below 60 kgs. were encountered and can be attributed to the variability of the shear tool positioning at the side of the die.

Figure 3.7 was the prevalent failure mode encountered at 85/85 exposure. This type of failure mode suggested that adhesion have been weaken greatly at the interface of die backside and paste. Moisture must have diffused in this interface faster rather than the interface of paste and paddle. Insufficient filleting coverage at the die corner accelerated the moisture diffusion.

The common failure mode of die shearing encountered in 121/100 and 135/85 environments is shown in Figure 3.8. In this type of failure mode, moisture affected both the adhesion at the two opposite interfaces of the paste, i.e., paste-die backside, and paste-paddle.

3.3 Time-to-failure Model Equations

Equation (4) is the model equation for predicting time to failure in the presence of physio-chemical process or processes that lead to the device failure. The temperature and relative humidity dependency of time-to-failure is modelled in the following expression:

$$t_f \cong A\ (\%RH^n\ \exp\ (\Delta E/kT) \qquad \text{Eqn.(4)}$$

where:
ΔE = activation energy; and
n = the measure of moisture dependence of the failure

From the trendline equations, the time of exposure corresponding to shear strength failure is determined when the critical value for the die shear strength is specified. These values are used in the calculation of the A, n, and ΔE.

The critical shear strength specification depends mainly on the die area. For Mil Standard 883, an upper limit of 5.0 kgs. applies for the 64 x 10^{-4} in.^{2} or greater die area. For the purpose of the study, the time-to-failure model equation is developed to predict the 10 kgs. die shear strength failures at different environments. Hence,

$$t_{10} = A(\%RH)^n\ \exp\ (\ \Delta E/kT) \qquad \text{Eqn.(4a)}$$

where t_{10} is the time of exposure to condition of RH and T until shear strength become 10 kilograms.

3.3.1 Determination of ΔE

In order to determine the activation energy, Equation (4a) is rewritten as:

$$t_{10} = A'\exp\ (\Delta E/kT) \qquad \text{Eqn.(4b)}$$

$$\text{where } A'=A\ (\%RH)^{n}\ ,\ A = \text{constant}$$

Treating A' as constant, the natural logarithm transformation of both side results in a linear function:

$$\mathrm{In}\ t_{10} = \mathrm{In}\ A'+(\Delta E/k)^{*}\ 1/T \qquad \text{Eqn.(5)}$$

Using the t_{10} values computed using the trendline equations of 85/85 and 135/85, the linear plot of Eqn (5) provide a value for the slope from which the activation energy is calculated. The calculated value of the activation energy for the shear strength degradation due to moisture is 0.362 eV. The activation energy for moisture saturation in the molding compounds has a reported[12] value of 0.4 eV. Further work has shown the activation energy for moisture saturation in silver paste epoxy to be the same[11].

3.3.2 Determination of n and A

Equation (4a) transforms into Equation (4c) when A and T are treated as constant, and the %RH as the only variable. Mathematically,

$$t_{10} = B'\ (\%RH)^{n} \qquad \text{Eqn.(4c)}$$

where

$$B' = A\ \exp(\Delta E/kT) \qquad \text{Eqn.(6)}$$

Taking the natural log transformation of Equation (4c), a linear function with the following form is derived:

$$\mathrm{In}\ t_{10} = \mathrm{In}B'+n\ \mathrm{In}(\%RH) \qquad \text{Eqn.(7)}$$

Using the t_{10} values from the 85/85 and 85/60 trendline equations, Equation(7) allows the determination of the value of n which is the slope of the linear plot of ln t_{10} against ln (%RH).

From the intercept, ln B', the value of B' is known. With known B', and T held as constant at 358°K (85°C), the relationship in Equation (6) will give the value of A.

The calculated value of A was in the order of 10^{-5}; whereas, n was about seven times the quoted value from the work of D.S. Peck. A big value of n shows that %RH has a tremendous effect as far as the die shear strength is concerned. Table II compares the time-to-time, t_{10} values calculated from the trendline and model equations.

Table II. t_{10} values (in hours) for different exposure environments.

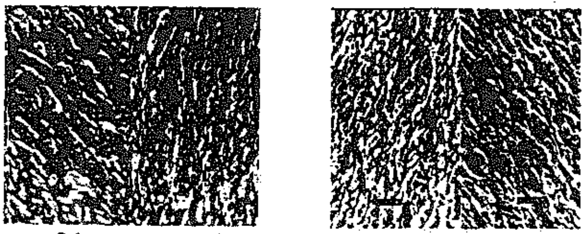
T°C/%RH	t_{10} from Trendline	t_{10} from Model	% Error
85/85	57.78	58.98	0.35%
135/85	13.81	13.72	0.65%
85/60	205015.00	204404.00	0.30%
20/70		74752.00	
25/55		16×10^{6}	

Table II shows a close prediction of the time to failure (die shear strength of 10 kgs.) at two temperature values with %RH=85%. The negligible percent error may indicate that the model is reliable within the range considered. The errors are expected to become large in worst conditions since, in this case, trendline and model equation predicted small values for the shear strength. In addition, error in the prediction in harsh condition may be due to different mechanisms that may not be present in the less stringent conditions.

3.4 SEM Inspection

Samples from the moisture absorption experiment were subjected to SEM inspection in order to compare the effect of moisture at different environments. Likewise, the change in the morphology of the paste surface after exposure will give indication of the extent of reaction. SEM photographs in Figure 3.9 show the differences in external morphology of samples exposed at 85°C/85%RH environment. SEM inspection found the paste exposed at 1 to 20 hours did not show any much difference compared to that of unexposed paste which is similar to one shown in the left of Figure 3.9a - the sample exposed for 2 hours. Paste exposed for 42 hours and longer (84 and 168 hours--Figure 3.4lb) were the only ones to give the distinct difference. It can be observed that the depressions or pits are very noticeable as a sign of decomposition or "erosion" after long exposure. This indicate removal of material from the surface of the paste brought about by moisture exposure.

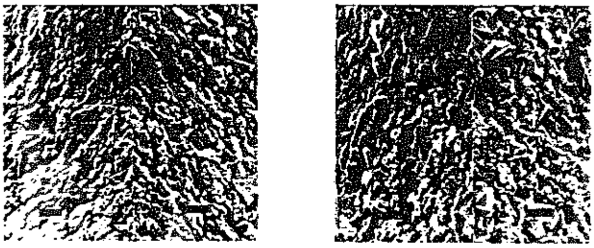
Samples from the 135°C/85%RH experiment were also observed to show increasing degree of paste "erosion" as exposure duration is lengthened. Samples exposed as early as 10 hours showed noticeable texture differences in the SEM photographs. The morphology of paste surface exposed for 42 hours (In Figure 3.9a) is worst compared to the one exposed at 85/85 environment for 168 hours. Photographs of 84th and 168th hours-exposed samples revealed the fillers of the paste, with the latter showing gross material removal from the surface. Additional work is currently being undertaken to determine the mechanism of this "erosion" degradation.



2 hrs 42 hrs
a.

84 hrs 168 hrs
b.

Figure 3.9 Surface texture of the paste exposed to 85°C/85% RH environment (1500x)



2 hrs 42 hrs
a.

84 hrs 168 hrs
b.

Figure 3.10 Surface texture of the paste exposed to 135°C/85% RH environment (1500x)

3.5 IR Analysis

Infrared Spectroscopy methods can be used to investigate bond formation or disappearance. The different modes of atomic bonding vibration produced peaks in the IR spectrum distinctive of the chemical compound. Those distinct peaks are considered as fingerprints especially of organic compounds. From the IR spectrum, the identities and behavior of atomic bonding of the compound, and its concentration, can be deduced. Table III[12] are the common functional groups and their corresponding energies.

Table III. Common functional groups

Functional Group	Frequency, cm^{-1}
OH Alcohol	3580-3650
H-Bonded	3210-3550
Acid	2500-2700
NH Amine	3390 (antisymmetric) 3200 (symmetric)
CH Alkane	2850-2960
Alkene	3010-3095
Alkyne	3300
Aromatic	3030 (approx)
C=0 Aldehyde	1720-1740
Ketone	1675-1725
Acid	1700-1725
Ester	1720-1750
C N Nitrile	2000-2300

The uncured, cured, and moisture exposed paste were subjected to IR to confirm water incorporation in the cyanate ester structure. Figures 3.11 to 3.13 are the spectra gathered from the samples.

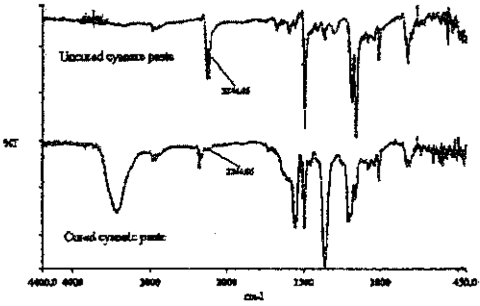


Figure 3.11 IR spectra of cured and uncured paste

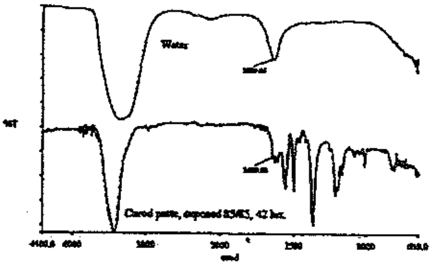


Figure 3.12 IR spectra of water (top) and 42th hour sample, 85/85

The IR spectra of uncured and cured paste is presented in Figures 3.11. The peak at 2214 cm-1 of the uncured paste disappeared after curing. This peak belongs to the cyanate esterphenol monomer bonds which are destroyed upon heating of the uncured paste. Upon curing, cyanate ester monomers poly-merize to form three dimensional triazine rings1. The peak appearing at about 1550 cm-1 is associated with the triazine rings formed. The peak at about 3500cm-1 in the cured paste can be water which was absorbed after curing stage.

The spectra of water is shown in Figure 3.12. The peak at 3300 cm^{-1} is due to the stretching oscillation of the O-H bonds while the one at 1629 cm^{1} is brought by the bending frequency of the O-H bonds. The peaks appearing at the right side of the spectrum represent the signature IR peaks of cured cyanate-ester paste.

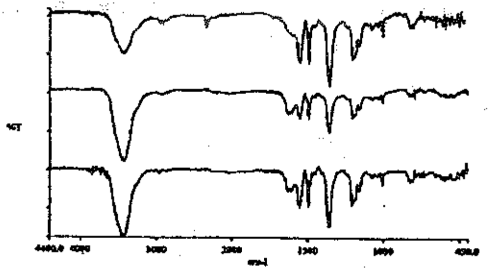


Figure 3.13 IR spectra of cured paste, (top) 85°C/85% RH samples exposed for 20 hours (middle), and 42 hours (bottom)

Figure 3.13 shows spectra of the cured paste, and the samples exposed at 85/85 environment for 20 and 42 hours. The emergence of the water peak 1629 cm^{-1} in 20th hour sample which clearly stand out in 42nd hour sample is an evidence of water "incorporation" in the paste structure. The non-symmetric side appearing at 3300 cm-1 peaks indicates the presence of amine.

Figures 3.14 and 3.15 are the IR spectra of 84th and 168th hour samples, respectively, exposed in 135/85 environment. These two spectra also reveal increasing water peak at 1629 cm. This further proved that water "trap" or "fixed" in the structure is increasing as the exposure is lengthen.

The peak for the R-NH2 (amine) is not distinct in the spectra gathered from 85/85 samples. Nevertheless, exposure in 135/85 environment did produce sufficient change for the amine peak to be visible in the IR spectrum. The spectrum of 168th hour reveal the amine peak at 3200 cm^{-1}. The amine peak is highlighted in Figure 3.15.

The IR analysis verified three important points. First, the data revealed that water is indeed incorporated in the structure of the paste. This incorporation of water is increasing with longer exposure as evidenced by the increasing IR peak at 1629 brought about by the bending oscillation of the O-H bonds. Secondly, the absence of alteration of the signature peak of the cured paste hinted that chemical rearrangement did not occur at the temperature range considered. Thirdly, amine as reaction product was confirmed to be present in the 135/85 sample.

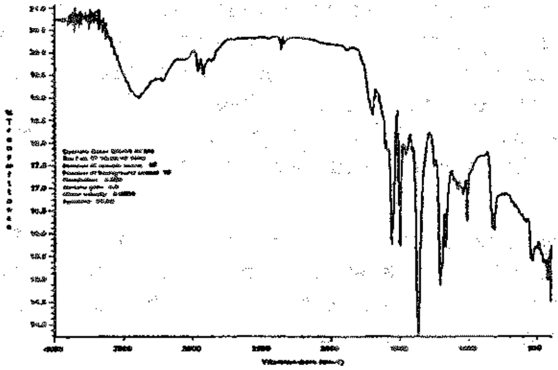


Figure 3.14 IR spectrum of 135/85 sample, exposed for 84 hours

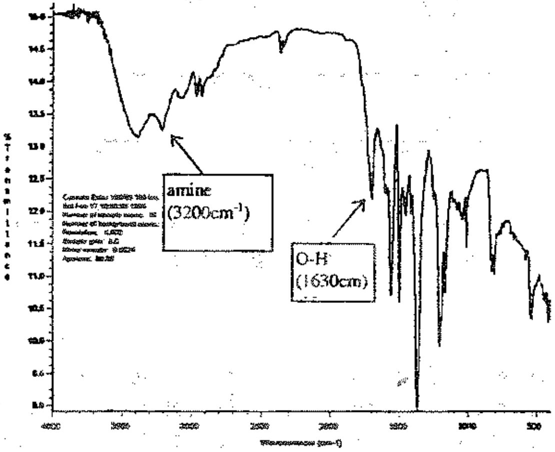


Figure 3.15 IR spectrum of 135/85 sample, exposed for 168 hours

4.0 CONCLUSIONS

The following conclusions are formulated based on the results of this study:

1. The moisture absorption behavior of the LTDA initially exhibits weight loss before further exposure could provide a significant weight gain. The total moisture gettering capacity is considerable when compared with silver-epoxy paste.

2. The LTDA exhibited "physical" erosion during long term exposure to environments more severe than 85°C/85%RH.

3. The IR analysis confirmed the water "incorporation" in the LTDA, which increases with prolonged sample exposure. IR spectra of the samples showed no major peak formation and changes indicative of significant structural change.

4. Die shear strength degrades to critical level at fast rate in harsh conditions (>85°C/85%RH). The die shear strength behavior at 85/60 conditions revealed no reliability concern even after 168 hours exposure. The model equation predicted the time to failure at shop floor environment (25°C/55%RH) to be in the order of 10^6 hours.

5.0 ACKNOWLEDGEMENTS

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