

Low Outgassing and Ionic Content, High-Performance Light and Moisture Dual-Curable Conformal Coating

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Abstract

Polymeric conformal coatings are used to improve and extend the reliability of printed circuit boards against environmental conditions. There is high interest in using light-curable conformal coatings due to their process benefits over conventional technologies, including the ability to use a non-solvated material, higher throughput, space savings, and lower operating costs. Light and moisture dual-curable conformal coatings were developed to ensure the curing of the coating even if the material flows underneath components on circuit boards.

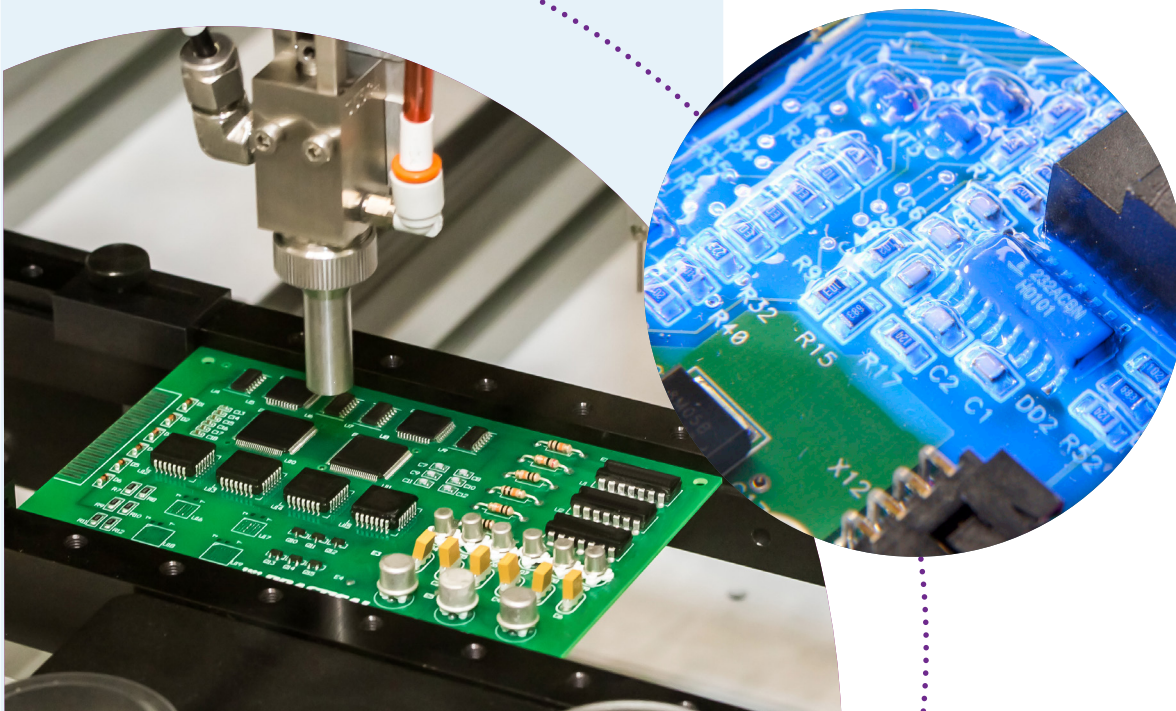
The use of light-curing coatings in aerospace and defense applications has been limited due to stringent low ionic content (MIL-STD 883 method 5011.7) and low outgassing (ASTM E595) requirements. A recently developed technology enabled formulation of a coating that meets these requirements without giving up the process benefits of the light and moisture dual-cure conformal coatings as well as the resistance properties.

In this paper, the ionic content, outgassing, and reliability testing such as heat and humidity (85°C, 85% relative humidity), sequential thermal shock and cycling (-65°C to +150°C), and salt spray corrosion resistance will be discussed. These results are compared against "out-of-kind" conventional conformal coatings used in the aerospace and defense industry and an "in-kind" light- and moisture- curable conformal coating.

Introduction

Conformal coatings are thin coatings that are applied to printed circuit boards (PCBs) and components mounted on them to protect against environmental conditions. The use of conformal coatings becomes necessary as the size of the parts decrease and the gap between components or the gap between features of the components decrease. Conformal coatings provide electrical insulation between components or features of the components, provide increased mechanical support, and hence allow design of smaller, more dense PCBs.^{[1], [2], [3]} The typical thickness of the conformal coatings varies between 25µm to 225µm. The coating can be applied by a variety of methods, such as dipping, brushing, spraying, and flow coating. For light curable technologies, it is most common to spray the coating to a desired thickness.

There are different types of conformal coatings which are typically classified by their chemistry. Acrylic and polyurethane-based conformal coatings often require the use of more than 50% solvents by weight, particularly to adjust viscosity for their application. Polyurethane conformal coatings provide good chemical and moisture resistance but are often hard to rework and create problems during application in humid environments. Acrylic conformal coatings are easy to rework but have poor chemical resistance. Both acrylic and polyurethane conformal coatings were the coatings approved in early aerospace and defense applications. They require layer-by-layer application to reach the required thickness and need evaporation of the solvent



after application of each layer. These solvated conformal coatings have operating range, which is limited due to their thermoplasticity, causing the material to soften and flow at elevated temperatures.

Silicone conformal coatings are often preferred for very high and low-temperature environments. They are required to be used as two-part with a short pot life or require thermal curing. Similar to silicones, epoxy conformal coatings are often applied as two-part systems with limited pot life or needing to be cured at high temperatures. Poly-para-xylylenes, commonly known as parylenes, are used in demanding aerospace & defense applications. The use of parylenes is limited since they require a chemical vacuum deposition application at an extremely high temperature with a vacuum coating process, therefore, it is challenging to obtain high throughput and they cost significantly more compared to other technologies.^[4]

Light-curable coatings do not require solvent dilution or evaporation and they can be applied to desired thickness in only one coating layer. Light curing provides on-demand instant cure and enables a smaller footprint on the manufacturing floor. There is no need for mixing, as with two-part coatings; no need for explosion-proofing, as with solvent-based materials; and typically, fewer steps and fewer operators are required for each processing step.^{[5][6]} In addition, no extra shipping charges are required as the case with coatings containing solvents. Light curing is also an ideal technology for heat-sensitive substrates.^[7]

Two types of polymerization mechanisms are predominantly used in light-curing: free radical and cationic polymerizations. Photopolymerization mechanism steps are depicted in Figure 1. Photoinitiators absorb light and then generate free radicals or cations that are capable of initiating polymerization of other ingredients of the formulations. During this process, the excited state of the photoinitiator may be quenched by atmospheric oxygen or water depending on the type of polymerization mechanism. Rate of polymerization depend on the type and efficiency of the photoinitiator photoinitiator. The Polymerization rate cannot be increased simply by increasing photoinitiator concentration because a higher amount of the photoinitiator will also block the penetration of light into lower sections. Therefore, photoinitiator concentration would need to be optimized. The polymerization rate can also be adjusted by changing the light intensity.^[8]



Figure 1. Polymerization Steps in Light Curing

The free-radical curing mechanism is used in most conformal coatings due to its ability to obtain a wide range of range of physical properties. Typical ingredients of free radical light-curable formulations and their functions are represented in Figure 2. The physical properties of the light-curing materials mostly depend on the oligomers and monomers used in the formulations. Monomers are usually introduced as a reactive diluent to adjust viscosity and physical properties.^[9] Rigid or highly flexible elastic materials can be obtained by choosing the appropriate combination of monomers and oligomers.

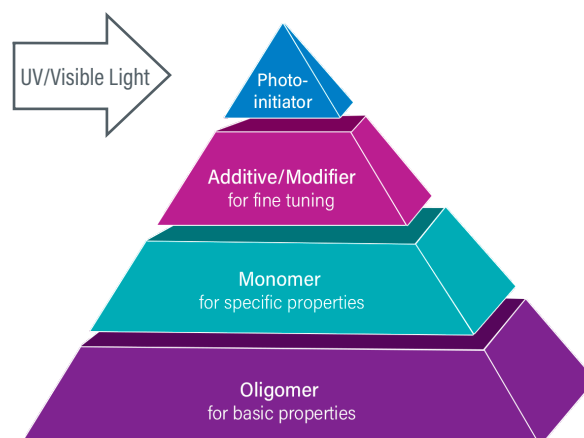


Figure 2. Ingredients of a Typical Light-Curable Product

A limitation of light-curing is the curing of shadow areas where light cannot penetrate. Selective dispensing can be used to avoid material flowing into shadow areas, but it would not eliminate the limitation and restrict the use of light-curing in wide range of applications. Light/heat dual-curing and light/moisture dual-curing conformal coatings have been developed to allow curing in shadow areas that is present on PCBs.^[9] In light and moisture (LM) dual-curable formulations, moisture curing acts as a secondary curing mechanism and enables the curing of materials in shadow areas over time with atmospheric moisture.

Experimental

Viscosities of the liquid coating formulations were measured per ASTM D2556. Ionic contents of coatings were measured in accordance with MIL-STD 883L method 5011.7 section 3.5.4 and 3.8.7. Total ionic content and hydrogen ion content were determined by analyzing water extraction samples of cured coatings with a two-channel pH/conductivity measuring instrument. Specific ion contents were measured via analysis of the water extractions of cured coating samples with an ultra-high performance liquid chromatograph (UHPLC) equipped with anion and cation columns. Thermal analysis of coatings was performed with a thermogravimetric analyzer using 10°C ramp rate in accordance with MIL-STD 883L method 5011.7 section 3.8.5.1 and ASTM D3850. Percent weight loss of coatings were reported at 200°C. Wetting of different substrates by uncured liquid conformal coatings was evaluated based on ASTM D724 utilizing a Goniometer. The contact angle formed between a drop of conformal coating and each substrate was reported. Dynamic mechanical properties were measured at 1 hertz frequency with a dynamic mechanical analyzer (DMA) according to ASTM D5026.

Conformal coatings were applied to boards by precision spraying to obtain 75 to 90 μm dry film thickness. Light-curable formulations were cured with mercury-based broadband light (2,500 mW/cm^2 light intensity at 1.2 m/min conveyor belt speed). Figure 3 shows curing in a light conveyor. After the light curing, secondary moisture curing formulations were kept at 25°C, 50% relative humidity (RH) for 7 days to complete moisture cure. Solvent based conformal coatings were air dried at 25°C, 50% RH for 7 days. Secondary heat curing formulations were cured in an oven at 120°C for 30 minutes following the light curing.

Custom designed multi-pattern FR4 boards as shown in Figure 4 were used to evaluate damp heat and salt spray corrosion resistance. A humidity chamber was set to 85°C, 85% RH for 1000 hours to evaluate damp heat resistance of the coatings. Salt spray corrosion resistance was evaluated using ASTM B117. Coated boards were exposed to 5% sodium chloride solution at 35°C for 1000 hours in a salt spray chamber. Upon completion of the reliability tests, samples were maintained at 25°C, 50% RH for a 24-hour stabilization period and visually inspected for the appearance, crack or delamination of the coatings and corrosion on the copper by a digital microscope. Coated boards were subjected to a modified voltage transient test before and after reliability tests according to UL-746E.^[6] 10 pulses of 6kV voltage were

applied to the boards over 2 minutes. There should be no disruptive charge formation evidenced by spark-over or flash during the voltage transient test. Sequential thermal shock and temperature cycling tests were performed on populated test boards given in Figure 4 following MIL-STD 883 methods 1010 and 1011 at test condition C. For thermal shock testing, coated boards were exposed to 15 cycles of -65°C and +150°C with 5 minutes dwell time at each temperature and 10 second transition time between lowest and highest temperatures. The boards exposed to thermal shock resistance were then exposed to 100 cycles of temperature cycling between to -65°C and +150°C with 10 minutes dwell time at each temperature and 13 second transition time between lowest and highest temperatures. Any cracks or fluorescence loss of coatings on and around the components were inspected with magnification under UV-A light equipped with 365nm lamp.

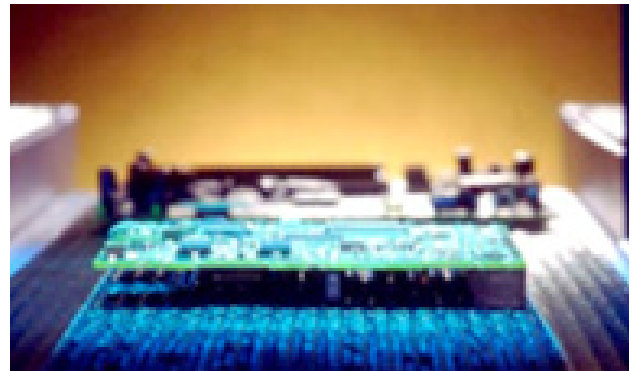


Figure 3. Light curing of coatings in a conveyor



Figure 4. Multi-pattern FR4 test coupon and populated test board

Results and Discussion

The use of conformal coatings is essential for PCBs used in aerospace & defense applications due to higher reliability standards compared to other electronics applications. The demand to reduce the weight and size of parts continue to increase as well as the demand to improve reliability and increase the range of operating temperatures. Acrylic and polyurethane conformal coatings have challenges in meeting the reliability requirements of most of the A&D applications. Light and moisture (LM) dual curing conformal coatings are appealing options due to ability to improve reliability, increase throughput and reduce footprint. Secondary moisture curing enables cure of the material seeping into shadow areas by utilizing atmospheric moisture without requiring special conditioning before proceeding to the next processes after light curing.

Meeting the exceptionally low ionic content and outgassing requirements of aerospace & defense applications are the major challenges for the light curable conformal coatings. Lowering the ionic content and

outgassing without giving up on fast processing and good reliability performance of LM dual curing conformal coatings were the main purposes of this work. Chemical classification, curing mechanism, and nominal viscosities of the conformal coatings tested are given in Table 1. The coating designated as LM1 is the new coating that was developed to obtain low ionic content and outgassing. LM2 was used as an "in-kind" benchmark since it is an LM dual curing and belongs to the same urethane acrylate chemical classification as LM1. Light and heat curable formulations, LH1 and LH2 were used as benchmarks since they are part of the urethane acrylate classification but utilize heat instead of moisture as the secondary curing mechanism. Solvent-borne (~40% solids) commercial conformal coatings based on acrylic (SA) and polyurethane (SP) chemistry known to be used in aerospace and defense applications were also tested as "out-of-kind" benchmarks.

Total ionic content (specific electrical conductance) and hydrogen ion content (pH) as well as the specific ion contents of the coatings are given in Table 2. The requirements to meet the MIL-STD 883 method 5011.7

Table 1. Description of the Conformal Coatings Tested

	Chemical Classification	Curing Mechanism	Viscosity (cP)
LM1	Urethane Acrylate	Light + Moisture	820
LM2	Urethane Acrylate	Light + Moisture	1100
LH1	Urethane Acrylate	Light + Heat	2300
LH2	Urethane Acrylate	Light + Heat	160
SA	Acrylic	Air drying	200
SP	Polyurethane	Air drying	200

are also given. The ions without a content requirement are also reported in Table 2. Although all the coatings evaluated met the specific ionic content requirements, LM1 and SA were the only coatings meeting the total ionic content and pH requirements. LM2, LH1, LH2, and SP, had higher total ionic content and lower pH compared to the requirements. The in-kind benchmark, LM2 had the worst results among the coatings. LM1 showed significantly better results compared to LM2. Raw materials such as oligomers, monomers, and additives used in regular light curable coatings, whether they have a secondary curing mechanism (such as moisture or heat) or not, affect the ionic impurity content of the coatings. LM1's constituents were optimized to obtain low ionic impurities and a balanced pH.

Polymeric coatings can lose weight as result of outgas of uncured ingredients or impurities. This can be a concern for A&D applications since outgassed ingredients might contaminate other surfaces. Therefore, it was crucial to

design a coating that can pass MIL-STD 883 method 5011.7 thermal stability test and ASTM E595 outgassing test. Among these tests, the less complicated thermal stability testing utilizing thermogravimetric analysis was used to screen all the coatings. Table 3 provides the weight loss data of the coatings at 200°C. Only LM1 and SA were able to meet the less than or equal to one percent weight loss requirement. LM1 and LM2 were also tested for ASTM E595, total mass loss and collected volatile condensable materials from outgassing in a vacuum environment. The results are displayed in Table 3. Similar to the thermal stability weight loss testing, LM1 showed significantly better results compared to LM2 and was able pass the requirements. Developing a low ionic content conformal coating that can pass low outgassing requirements was encouraging since it could help in obtaining a cleaner PCB assembly and hence provide improved reliability. The rest of the project was then focused on accelerated reliability tests.

Table 2. Ionic content of coatings

	LM1	LM2	LH1	LH2	SA	SP	Requirements
Total ionic content (mS/m)	3.60	27.82	7.26	12.57	0.26	7.83	≤ 4.50
Hydrogen ion content, pH	4.13	3.14	3.77	3.53	5.53	3.79	4.0 ≤ pH ≤ 9.0
Chloride (ppm)	1	5	0	2	0	4	≤ 200
Sodium (ppm)	0	49	44	5	19	42	≤ 50
Potassium (ppm)	3	14	5	0	3	13	≤ 50
Fluoride (ppm)	0	0	0	3	1	0	≤ 50
Bromide (ppm)	0	0	0	0	0	0	-
Nitrate (ppm)	15	15	9	8	0	0	-
Phosphate (ppm)	2	931	0	0	0	0	-
Sulfate (ppm)	0	19	0	8	0	0	-
Ammonium (ppm)	11	16	11	21	5	5	-
Lithium (ppm)	0	0	0	0	0	0	-
Magnesium (ppm)	0	0	0	0	0	0	-
Calcium (ppm)	0	0	0	0	0	0	-

Table 3. Thermal weight loss of coatings

	LM1	LM2	LH1	LH2	SA	SP	Requirement
Weight loss at 200°C (%), MIL-STD 883	0.67	1.81	2.12	2.81	0.25	1.87	≤ 1%
Total weight loss, ASTM E595 (%)	0.90	3.15	-	-	-	-	≤ 1%
Collected volatile condensables, ASTM E595 (%)	0.02	0.54	-	-	-	-	≤ 0.1%

For reliability testing the focus was given on comparing performance of LM1 against LM2 as in-kind benchmark and SA and SP as out-of-kind benchmarks. Good wetting of substrates is a crucial property for conformal coatings to obtain good adhesion, avoid defects and improve reliability. Contact angle measurement at various substrates were used to quantify wetting of the conformal coatings. The average of contact angle values measured were reported on Table 4. LM coatings provided lower contact angles compared to SA and SP.

Predicting reliability performance of conformal coatings is important for not only development of high-performance conformal coatings but also quality assurance purposes. Rigid conformal coatings can cause stress on components or solder joints or crack themselves due to thermal expansion or contraction during thermal shock or temperature cycling. Dynamic mechanical analyzer (DMA) is an instrument that is used extensively to characterize change in a material's properties with temperature. During DMA testing oscillating force is applied at a set frequency to a coating film and the material's deformation response is measured as the force applied and released. Materials' elastic response is often characterized by storage modulus which is a measure of how much force needs to be put into a sample to distort it. Therefore, higher storage modulus

materials could help in performance of the coating at elevated temperatures by providing more resistance to deformation. On the other hand, lower storage modulus materials may apply less pressure or have less tendency to crack with sudden temperature changes especially as the material cooled down to sub-zero temperatures. Glass transition temperature is the temperature where material transitions from a glassy state to a rubbery state. Polymers act significantly differently above and below their glass transition temperature including how much they expand or contract with thermal changes. Materials are often designed to avoid glass transition temperatures coinciding with daily operating temperatures of their use.

Dynamic mechanical properties of the light cured materials are given in Table 5. DMA was performed up to 90°C for SA and SP since they significantly soften at high temperatures due to their thermoplastic nature. SA has the lowest glass transition temperature (T_g) and storage modulus at every temperature which might help in performance of it against cold temperature exposure but might result in failure at higher temperatures. LM1 is designed to have higher storage modulus at elevated temperatures to have improved performance at high temperatures. It has similar T_g, and slightly lower storage modulus at -40°C compared to LM2.

Table 4. Average contact angle values measured on solder masks and chips

	LM1	LM2	SA	SP
Average Contact Angle on Solder Mask (°)	23	25	41	53
Average Contact Angle on Chips (°)	24	29	44	55
Average Contact Angle on Copper (°)	23	29	49	48

Table 5. Dynamic mechanical properties of light cured materials

	T _g (°C)	Storage Modulus (MPa)			
		at -40°C	at 25°C	at 85°C	at 165°C
LM1	67	2270	1210	8.6	5.2
LM2	65	2440	1210	2.8	3.0
SA	48	1810	490	0.4	-
SP	65	2190	900	1.9	-

Secondary moisture curing of the light cured conformal coatings enable cure of shadow areas on PCBs over time with ambient moisture. Table 6 lists tack free time of the coatings cured just with moisture under dark conditions. Both LM1 and LM2 were moisture curing within 24h to provide tack free surface without any light curing.

Table 6. Tack Free Time of the conformal coatings cured only with moisture

	LM1	LM2
Tack Free Time at 25°C, 50% RH	<1 day	<1 day

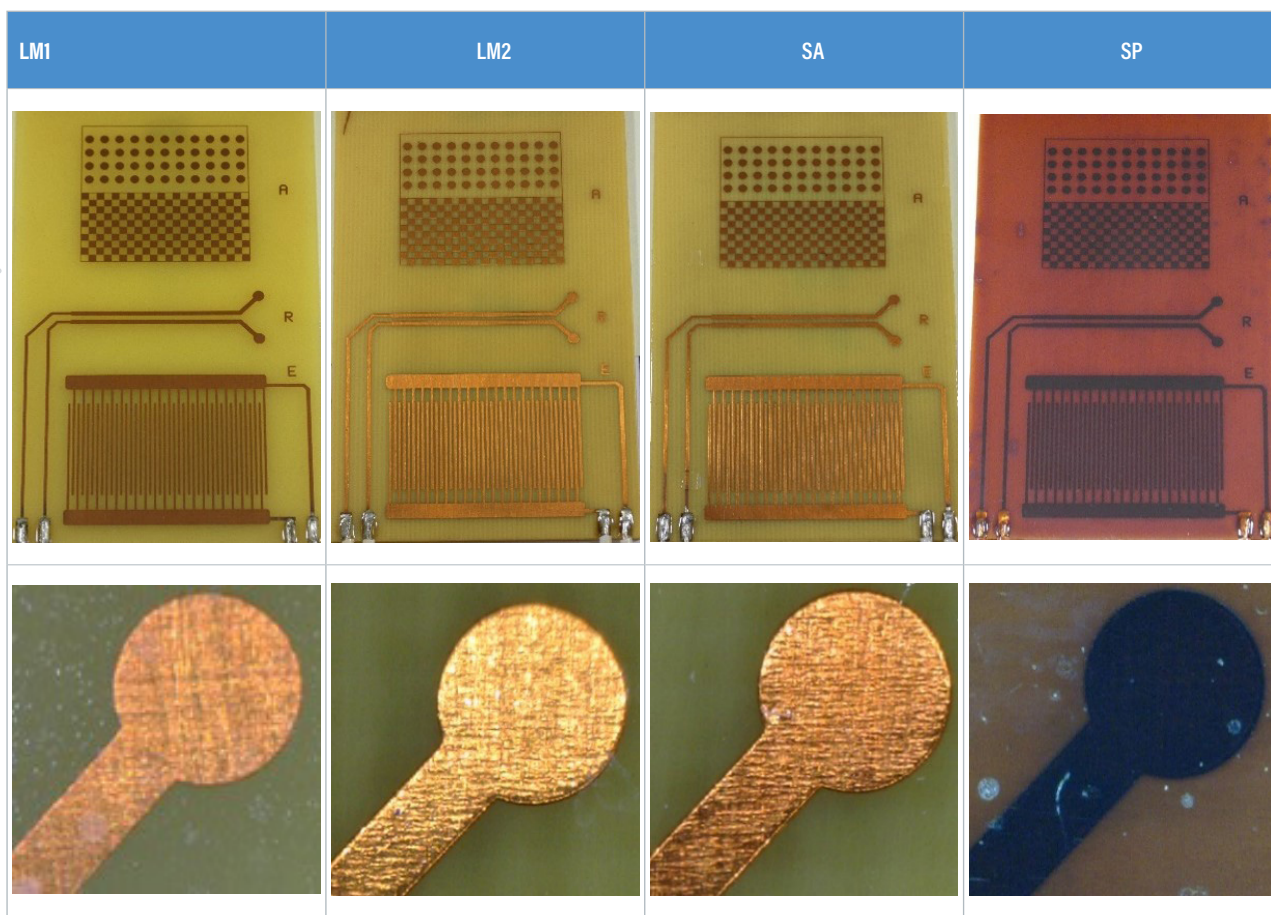
Photos of the multipurpose patterned boards with conformal coatings after they are exposed to 85°C, 85% RH damp heat reliability testing for 1000 hours are shown in Table 7. None of the coatings showed delamination or cracking. LM2 was the best performing coating after the damp heat test. LM1 was the second-

best coating in terms of protecting the copper. SP coating performed the worst as it became darker, and the copper underneath darkened significantly as shown in magnified image. There were several localized oxidation spots in SA.

Images of two of the boards for each coating after 1000 hours of salt spray corrosion resistance test are given in Table 8. The salt spray corrosion resistance test is correlated with permeability of the coating against salt and water and not allow them to reach the copper finish on the boards. SA performed the worst with showing large area corrosion starting from soldered leads. SP had several micro-oxidation spots but no major corrosion. LM1 and LM2 performed well with slight corrosion in one of the boards close to the soldered leads. LM2 had isolated corrosion in one of the boards which might be due to an application defect such as bubble entrapment rather than the coatings resistance to salt spray corrosion.

Thermal shock (-65°C to 150°C, 5-minute dwell time, 15 cycles) and temperature cycling (-65°C to 150°C,

Table 7. Damp Heat Reliability Test



10-minute dwell time, 100 cycles) tests were performed sequentially according to MIL-STD 883 method 1010 and 1011 on solder masked test boards that were populated with various chips. Table 9 shows magnified images under UV-A light of a selected part on the boards before and after the sequential testing. LM2 had performed the worst in terms of crack formation on the coating after the sequential testing. LM1 performed

well with no sign of cracking. SA's performance was also good with only one microcrack near a small part. SA and SP had shown thinning out over parts which is due to their thermoplastic characteristic. It was difficult to investigate the boards coated with SP after the sequential for cracks or even uncoated sections due to loss of fluorescence.

Table 8. Salt Spray Corrosion Resistance

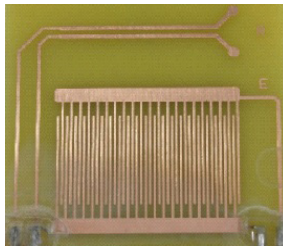
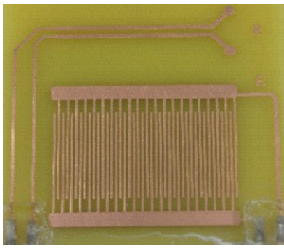
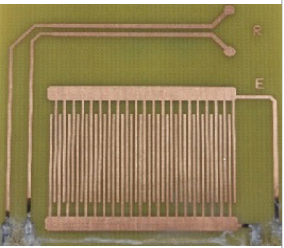
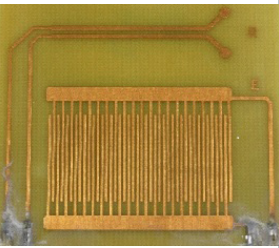
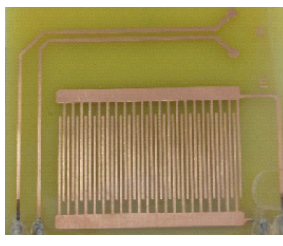
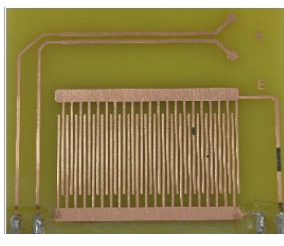
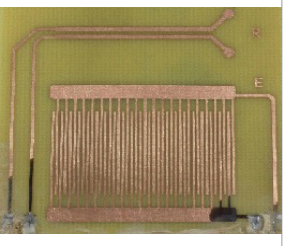
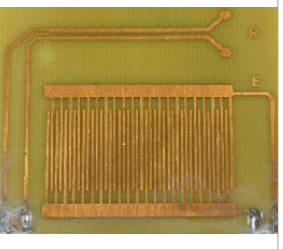
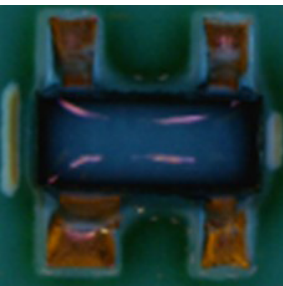
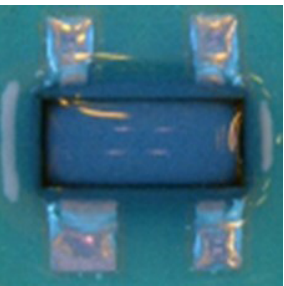
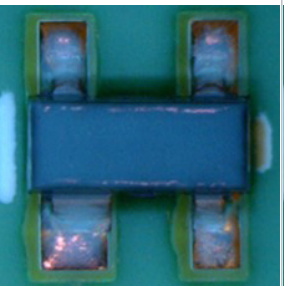
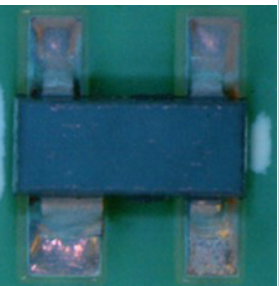
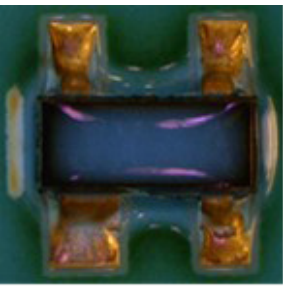
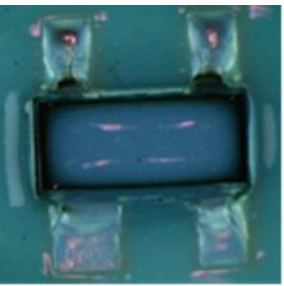
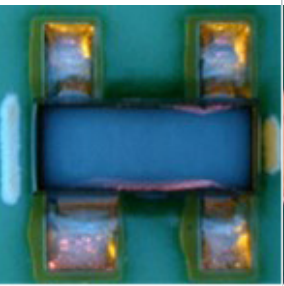
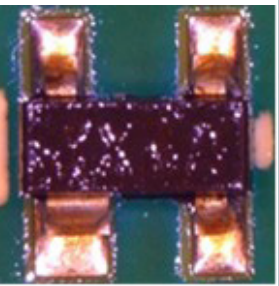
	LM1	LM2	SA	SP
Before testing				
After testing				

Table 9. Sequential Thermal Shock and Temperature Cycling Reliability Test

	LM1	LM2	SA	SP
Before testing				
After testing				

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Conclusion

Light and moisture dual-curable conformal coatings enable fast throughput and high reliability to PCBs. Their use in aerospace and defense applications was limited due to low ionic content and low outgassing requirements. The recently developed technology enabled formulation of light and moisture dual curing conformal coating with significantly lower ionic content and outgassing compared to the in-kind light and moisture curing coating benchmark. The new coating passed the critical low ionic content and thermal stability (MIL-STD 883 method 5011.7) and low outgassing (ASTM E595) tests. PCBs coated with the new coating outperformed the in-kind benchmark in sequential thermal testing. The new coating, as with the in-kind benchmark, quickly cures tack-free with moisture, allowing curing of the coating under shadow areas. It also showed good wetting properties and provided an excellent balance of reliability performance when compared with solvent-borne conformal coatings used in aerospace and defense applications. The benefits in performance are supplemented by the fact that this coating does not contain solvent and eliminates the need to evaporate solvents.



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