

High-Performance, Light and Moisture Dual-Cure Automotive Conformal Coating

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Abstract

Light-curable materials can provide significant benefits over conventional technologies, including lower operating costs driven by lower labor needs, space savings, lower energy demand, and higher throughput. A key advantage to light-curable conformal coatings is the ability to use a non-solvated “green” (100% solids) material. Conformal coatings are used to enhance long term reliability of automotive electronic parts. Key properties include resistance to rapid and extreme temperature changes, as well as protection against high heat-humidity, chemicals such as gasoline, and corrosive materials like salt and sulfur. We have developed a 100% solids conformal coating that is light and moisture dual-curable, and exhibits an excellent balance of properties and premium performance. Secondary moisture curing allows material under shadow areas to cure helping to eliminate concerns about uncured material on the printed circuit board (PCB). We will discuss the performance of this material when compared to other light-curable materials, as well as other chemistry types of conformal coatings, in reliability tests such as heat and humidity resistance (85°C, 85 % relative humidity), thermal shock resistance (-55°C to +125°C) and corrosion resistance (flowers of sulfur, salt spray and common automotive fluids). Any changes in physical appearance including any formation of oxidation spots was assessed, and electrical insulation performance was recorded both before and after reliability testing.

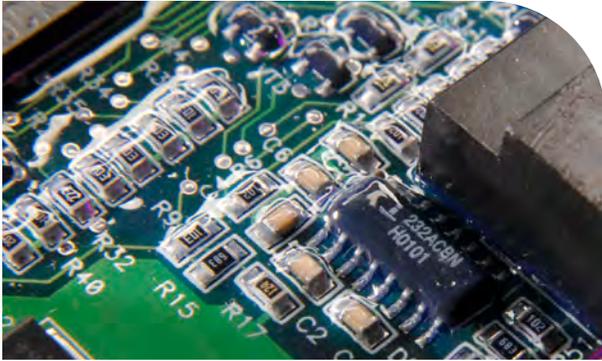
Introduction

Conformal coatings are thin coatings that are applied to PCBs to protect them against environmental conditions and to electrically insulate components. Conformal coatings allow for the design of smaller, more dense PCBs by allowing shorter spaces between conductors, increased mechanical support for components, and improved fatigue life of solder joints.^{1,2} Typical thickness of the conformal coatings varies between 25µm to 225µm. The coating can be applied by a variety of methods, such as by dipping, brushing, spraying, and flow coating. For UV-curable technologies, it is most common to spray the coating to a desired thickness.

The conformal coatings market is gradually growing, particularly as the use of electronics in automobiles is increasing. As the usage of electronic components in both under-the-hood and passenger compartments increases, the use of conformal coatings is also increasing.³ The usage of conformal coatings is not relegated only to automotive uses, but is also increasing in consumer electronics as the devices become smaller and as the consumers demand more water-resistant devices.

Conformal coatings are typically classified by their chemistry. Acrylic and polyurethane-based conformal coatings often require use of solvents, particularly to adjust viscosity for their application. Polyurethane

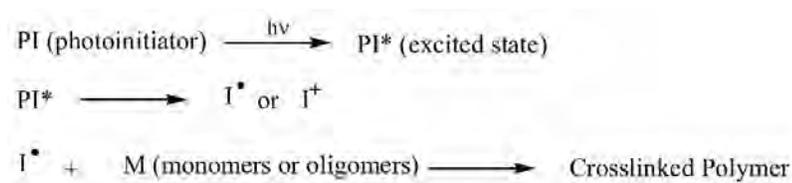
Figure 1. Light-Curable Conformal Coating



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. Silicone conformal coatings are often preferred for very high and low temperature environments, but they have relatively short pot life or require thermal curing. Epoxy conformal coatings are often applied as two-part systems with limited pot life. Poly-para-xylylenes are applied at very high temperature with a vacuum coating process, therefore, they cost significantly more compared to other technologies.⁴

Light-curable coatings' usage and application areas have steadily increased, since they do not require solvent dilution or high energy usage for solvent evaporation, and they allow for instant cure and improved productivity. In addition to saving time, light-cure technology also saves space on the manufacturing floor and increases efficiency overall. There is no need for mixing, as with two-part epoxies; no need for explosion-proofing, as with solvent-based coatings; and typically, fewer steps and fewer operators are required for each processing step.^{5,6} In addition, light curing is an ideal technology for heat-sensitive substrates.⁷

Figure 2. Polymerization Steps in Light Curing



The basic polymerization mechanism of light-curable conformal coatings is depicted in Figure 2. Photoinitiators convert light energy to chemical energy by absorbing the photons and generating free radicals or cations. Rate of polymerization and curing wavelength depend on the type, absorption wavelength, and efficiency of the photoinitiators. During this process, the excited state formed by absorption of light may be quenched by atmospheric oxygen. Therefore, top surface of the coating is often softer than the bottom part of the coating if the curing is carried out under air. The rate of polymerization can be increased by increasing the light intensity. Photoinitiators absorb the light and initiate the polymerization, but they also block the penetration of the light to lower parts. Therefore, to optimize the cure rate, photoinitiator concentration needs to be optimized.⁸

Light curing relies on light to initiate the polymerization. Therefore, a significant limitation of light curing is the curing of shadow areas where light cannot penetrate. Light and moisture dual-curing conformal coatings have been developed to allow cure in applications where shadow areas present on PCBs. Prior to the development of light and moisture dual-curing conformal coatings, shadow areas were managed by selective coating, i.e. eliminating the need to cure in shadow areas or by a light and heat dual-curing process. Users needed to balance the cost of selective dispensing equipment and time/energy costs of a secondary heat cure, that may have limitations due to the materials used on the PCB. Light and moisture curing conformal coatings enable cure of shadow areas on PCBs over time with moisture, which eliminates the need for a secondary heat curing or selective dispensing.

Experimental

Conformal coatings were applied by precision spraying to obtain a 75 μm (3 mil) dry film thickness. Light-curable formulations were cured with mercury-based UV light (2,500 mW/cm^2 light intensity at 1.5 m/min conveyor belt speed). Figure 3 shows curing in a UV conveyor. After the UV curing, formulations with secondary moisture cure were kept at 25°C, 50% relative humidity (RH) for 6 days to complete moisture cure. Alternatively, moisture cure can be accelerated at 40°C, 50% RH. Solvent-based conformal coatings were air dried at 25°C, 50% RH for 7 days. Custom designed multi-pattern FR-4 boards as shown in Figure 4 were used to test heat-humidity, thermal shock, and corrosion resistance.

Figure 3. Light Curing of Coatings in a UV Conveyor

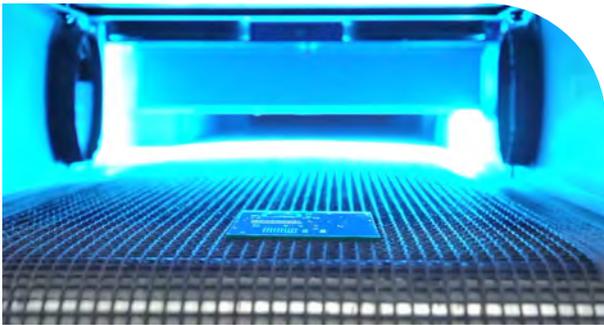
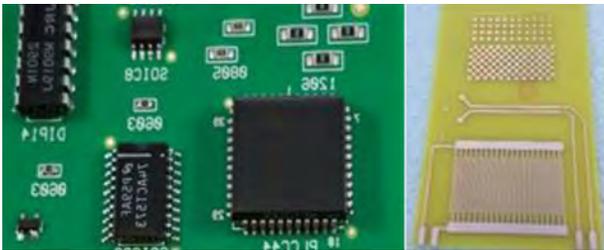


Figure 4. Multi-pattern FR4 test coupon and populated test board



A humidity chamber was set to 85°C, 85% RH for 2,000 hours to evaluate heat and humidity 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 1500 hours in a salt spray chamber. Flowers of sulfur corrosion resistance was tested using ASTM B809 whereby coated boards were suspended over powdered sulfur in a vented container shown in Figure 5 at around 90% relative humidity and 50°C temperature for 1300 hours.

Figure 5. Representation of a flowers of sulfur test 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 microscope camera. Coated boards were subjected to a modified voltage transient test before and after reliability tests according to UL-746E.9 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.

Thermal shock resistance was tested on populated test boards (Figure 3) by exposing coated boards to -55°C and +125°C with 30 minutes dwell time at each temperature and 15 second transition time between lowest and highest temperatures. The boards were tested under these conditions for 1,000 cycles. Any cracks or delamination of coatings on and around the components were inspected with magnification.

Wetting of substrates for a variety of 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. Adhesion of the coatings was tested on FR-4 boards masked with common solder masks by using the crosshatch adhesion test method in accordance with ASTM B2197. In addition, a Mandrel Bend Test per IPC-TM-650 2.4.5.1 was used to evaluate the flexibility and high temperature resistance of conformal coatings coated on 0.07 mm thick copper coupons before and after 180°C, 24h heat treatment. A 3-mm mandrel rod was used to bend the coated copper coupons to 180° within one second.

Viscosities of the liquid coating formulations were measured per ASTM D2556. Cured mechanical properties were measured per ASTM D638 and ASTM D2240. Glass transition temperature (T_g) values were determined utilizing dynamic mechanical analyzer

(DMA). Coefficient of thermal expansion (CTE) values were determined by using thermomechanical analyzer (TMA).

Results and Discussion

Light and moisture (LM) dual-curing conformal coatings have become the preferred choice of conformal coatings in many applications over the past decade due to elimination of a heat cure process. We recently developed a premium performance LM dual curing conformal coating (LM1) that can withstand the harsh reliability tests used in the automotive industry. Two different commercially available LM dual curing conformal coatings (LM2 and LM3) and a light and heat dual-curing conformal coating (LH) were tested against LM1. Solvent-borne (~40% solids) commercial conformal coatings based on acrylic (SA) and polyurethane (SP) chemistry were also tested as “out of kind” benchmarks. Description of the conformal coatings tested and their nominal viscosities are given in Table 1.

Physical properties of the light-cured materials are given in Table 2. LM2 was chosen as a comparative conformal coating, since it has a higher Young’s modulus, lower elongation, and higher tensile strength than LM1. LM3 and LH were chosen, since they are more flexible (higher elongation and lower modulus) compared to LM1.

Secondary moisture curing of the light-cured conformal coatings enables cure of shadow areas on PCBs over time with moisture. Rate of moisture cure is important for faster processing of the parts. Table 3 lists tack-free time of the coatings cured just with moisture under dark conditions. Both LM1 and LM2 were curing within 24h whereas it took more than a week for LM3 to become tack free with only moisture curing.

Magnified photos of the boards on two select patterns before and after they are tested for 85°C, 85% RH damp heat reliability are shown in Table 4. After 2,000 hours, none of the coatings showed delamination or cracking. Among the light cured coatings, materials with lower elongation

Table 1. Description of the conformal coatings tested

| | Chemical Classification | Curing Mechanism | Viscosity (cP) |
|-----|-------------------------|------------------|----------------|
| LM1 | Urethane Acrylate | Light + Moisture | 700 |
| LM2 | Urethane Acrylate | Light + Moisture | 100 |
| LM3 | Urethane Acrylate | Light + Moisture | 500 |
| LH | Urethane Acrylate | Light + Heat | 2000 |
| SA | Acrylic | Air drying | 200 |
| SP | Polyurethane | Air drying | 200 |

Table 2. Physical properties of light-cured materials

| | Tensile Strength, psi | Elongation, % | Young’s Modulus, ksi | Shore Hardness | Tg, °C | CTE, <Tg (µm/m/°C) | CTE, >Tg (µm/m/°C) |
|-----|-----------------------|---------------|----------------------|----------------|--------|--------------------|--------------------|
| LM1 | 2,300 | 23 | 41 | D60 | 58 | 84 | 193 |
| LM2 | 7,400 | 5 | 116 | D75 | 79 | 64 | 178 |
| LM3 | 2,100 | 45 | 26 | D60 | 74 | 98 | 181 |
| LH | 1,000 | 140 | 1 | D60 | 41 | 101 | 192 |

Table 3. Tack-free time of the conformal coatings cured only with moisture

| | LM1 | LM2 | LM3 |
|--------------------------------|--------|--------|---------|
| Tack-Free Time at 25°C, 50% RH | <1 day | <1 day | >7 days |

Table 4. Damp heat reliability test

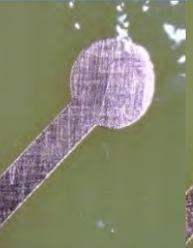
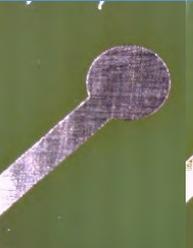
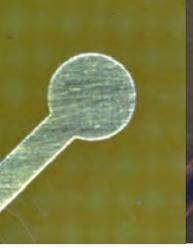
| | LM1 | LM2 | LM3 | LH | SA | SP |
|---------------|---|---|---|--|---|---|
| Initial |  |  |  |  |  |  |
| After 2,000 h |  |  |  |  |  |  |
| |  |  |  |  |  |  |

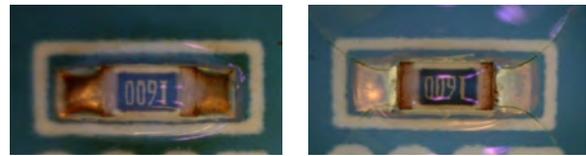
Table 5. Thermal shock reliability test

| | LM1 | LM2 | LM3 | LH | SA | SP |
|--------------------|---|---|---|--|---|---|
| Initial |  |  |  |  |  |  |
| After 1,000 cycles |  |  |  |  |  |  |

and higher modulus performed better. 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 became translucent with severe oxidation on copper as shown by Y-pattern in Table 4. On the copper of the board coated with LM3, there were distinctive oxidation spots formed. Although not as severe as the SP and LM3, LH and SA also showed high amount of oxidation. Boards coated with SA and SP and subjected to damp heat test also failed the voltage transient test.

Thermal shock reliability test was done both on the custom designed multi-pattern FR4 boards and solder masked test boards that were populated with various chips. After 1000 cycles, SP coating became translucent with severe oxidation on copper as shown by Y-pattern in Table 5. SA coating soften and delaminated. Both SP and SA coatings failed in the voltage transient test after thermal shock. No crack or delamination was observed with the rest of the coatings. On populated boards, LH performed the best with no crack or delamination. LM1 was the second-best performer with a few micro-cracks and no delamination or major cracks. LM2 delaminated from various places and had many major cracks and therefore performed the worst (Figure 6). LM3 showed no delamination or major cracks, but had more micro-cracks than LM2.

Figure 6. Thermal shock reliability test on populated boards: LM1 (left), LM2 (right)



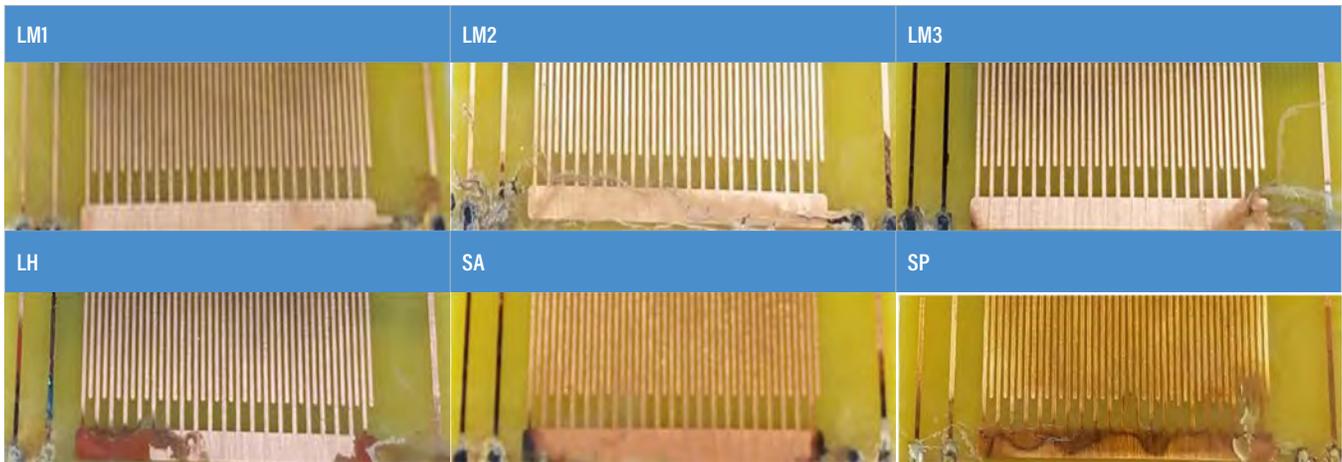
Magnified images of the boards on a select location before and after they are tested for flowers of sulfur (FoS) corrosion resistance are given in Table 6. The FoS test is correlated with porosity of the coating and its ability to avoid sulfur vapor to reach the copper finish on the boards. LM1 and LM2 did not show any sign of sulfur corrosion, whereas copper in LM3, LH, and SA showed severe corrosion. SP performed significantly better compared to the other solvent borne coating, SA. This might be due to the specific chemistry of SP (polyurethane) repelling the sulfur vapor.

Photos of the boards after 1,500 hours of salt spray corrosion resistance test are given in Table 7. The salt spray corrosion resistance test is correlated with permeability of the coating against salty water and not allow it to reach the copper finish on the boards. LM1 performed best in the salt spray corrosion test with no corrosion on the copper. LM2 was the second best performing one with slight corrosion on copper. Copper on the boards coated with the rest of the coatings had significant amount of corrosion.

Table 6. Thermal shock reliability test

| | LM1 | LM2 | LM3 | LH | SA | SP |
|---------------|-----|-----|-----|----|----|----|
| Initial | | | | | | |
| After 1,300 h | | | | | | |

Table 7. Salt spray corrosion resistance test



Chemical resistance tests were done by checking crosshatch adhesion of coatings after immersing coated copper coupons into various automotive fluids for 500h. In crosshatch adhesion test classification, 5B is given for the best adhesion result, which is for no coating removal during the test. Brake fluid (DOT 3) was the harshest of the fluids; none of the coatings could withstand it. LM1 along with the other light and moisture cure coatings (LM2 and LM3) provided perfect resistance to all the fluids except the brake fluid. LH failed from the ethanol resistance test in addition to brake fluid due to its low crosslink density and high flexibility. SA was the worst performing coating since it failed from four of the chemical resistance tests.

High-temperature resistance of coatings was evaluated by testing the mandrel bend resistance of the coatings on copper coupons and crosshatch adhesion on test boards after exposing them to 180°C for 24h. Mandrel bend testing was done to evaluate flexibility retention and crosshatch adhesion test was done to evaluate adhesion retention after high temperature exposure. LM1 had the best adhesion to the test boards after high temperature exposure. LM2 and SA failed the mandrel bend test whereas SP along with SA lost adhesion to the test boards after high temperature exposure.

Wetting of substrates is an important property for conformal coatings, especially applied at low thickness, to minimize coating defects such as pinhole and orange peel formation. Contact angle measurement at various solder masks and chips were used to quantify wetting

of the conformal coatings. The average of contact angle values measured on five solder masks and five chips were reported on Table 10. LH, SA, and SP provided higher average contact angle values whereas LM2 and LM3 gave the lowest contact angles.

Conclusion

High-performance conformal coatings are required to enhance the long term reliability of automotive electronic parts. The newly developed light and moisture curing conformal coating, provided an excellent balance of high performance properties when compared with other commercially available conformal coatings. This new coating quickly cures tack-free with moisture, allowing for curing of the coating under shadow areas. The new coating demonstrated excellent performance when tested against high temperature, humidity, and thermal shock, as well as resisting corrosion against flowers of sulfur and salt spray tests. It showed good wetting properties and performed admirably in high-temperature resistance and chemical resistance tests. The benefits in performance are supplemented by the fact that this material is 100% solids and therefore avoids the need to introduce any solvent materials.

Table 8. Chemical resistance test

| | Motor Oil | Transmission Fluid | Brake Fluid | Antifreeze | Windshield Cleaner | Power Steering Fluid | Ethanol |
|-----|-----------|--------------------|-------------|------------|--------------------|----------------------|---------|
| LM1 | 5B | 5B | 0B | 5B | 5B | 5B | 5B |
| LM2 | 5B | 5B | 0B | 5B | 5B | 5B | 5B |
| LM3 | 5B | 5B | 0B | 5B | 5B | 5B | 5B |
| LH | 5B | 5B | 0B | 5B | 5B | 5B | 0B |
| SA | 5B | 0B | 0B | 5B | 0B | 5B | 0B |
| SP | 5B | 5B | 2B | 5B | 5B | 5B | 5B |

Table 9. High-temperature resistance

| | Mandrel Bend Test after 180°C, 24h | Crosshatch Adhesion after 180°C, 24h |
|-----|------------------------------------|--------------------------------------|
| LM1 | Pass | 5B |
| LM2 | Fail | 4B |
| LM3 | Pass | 4B |
| LH | Pass | 4B |
| SA | Fail | 1B |
| SP | Pass | 1B |

Table 10. Average contact angle values measured on solder masks and chips

| | Average Contact Angle on Solder Masks (°) | Average Contact Angle on Chips (°) |
|-----|---|------------------------------------|
| LM1 | 35 | 42 |
| LM2 | 31 | 34 |
| LM3 | 34 | 39 |
| LH | 55 | 59 |
| SA | 41 | 47 |
| SP | 46 | 55 |

Acknowledgement

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