Identifying the cause of the growing phenomenon of discoloration and crisscrossing narrow dark lines on solar module surfaces.

太阳能组件表面日益渐增的变色现象和蜗牛纹的原因

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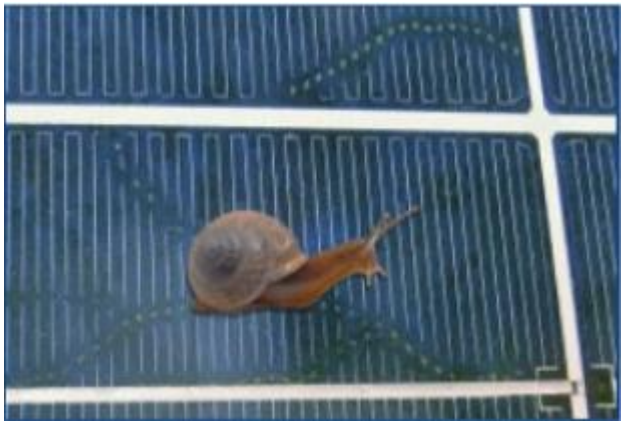


In recent years, the solar industry has been facing a mysterious phenomenon which experts have dubbed snail trail due to its unusual appearance. After a period of time ranging from several months to several years after initial installation, solar modules show some discoloration on the cells, and crisscrossing narrow dark lines about the thickness of a finger begin to appear on the surface of the modules. Snail trail has become a widespread phenomenon, with more than 13 module makers from around the world facing a similar technical obstacle. Although having carried out extensive research, there has not been identification of an exact culprit. However, Canadian Solar, one of the top five module manufacturers in the world, will identify the cause and proper steps to take to treat snail trail.

近年来,太阳能行业一直有一个难以解释的现象，由于其不寻常的外观而被专家们称作“蜗牛纹”。经过一段时间，从安装始几个月到几年不等,太阳能组件的电池出现变色, 大约一个手指粗的狭窄交错的暗线开始出现在组件的表面。蜗牛纹已经广泛出现,来自世界各地的超过13个组件生产商正面临类似的技术障碍。虽然进行了广泛的研究,但还没有找出确切的罪魁祸首。然而,阿特斯（加拿大研究中心）---世界顶级五大组件制造商之一,将确定原因并采取适当的措施处理蜗牛纹。

Based on Canadian Solar’s module manufacturing experience, snail trail happens very rarely - affecting very few modules, with the good news being that it does not appear to affect the output wattage. Testing of Canadian Solar’s modules with snail trail have been both internally by the Canadian Solar Photovoltaic Testing Laboratory and externally by the Frauenhofer Institute for Solar Energy Systems, a third-party Germany-based research organization, as well as in the field at a power plant. After extensive testing, the output performance reveals no significant drop in wattage, and

the drop exhibited by a very small number of modules was due to cell breakages instead of snail trail. Acceleration aging tests also occurred internally and externally. The reports show the snail trail does not spread after aging, and it does not affect the modules' long-term power output and reliability, echoing many other independent studies.

在阿特斯组件的制造经验中，很少发现蜗牛纹,仅影响到极少的组件。并且好消息是，蜗牛纹看来并不影响输出功率。阿特斯组件蜗牛纹的测试在内部阿特斯光伏测试实验室和外部第三方德国研究机构Frauenhofer同步展开。Frauenhofer是一个太阳能系统及电站研究所。经过大量的测试，输出性能显示无显著的功率下降，并且少数组件呈现的下降是电池的破损造成的,而不是蜗牛纹。同时，内部和外部也进行了加速老化试验。报告显示蜗牛纹在老化后不会蔓延,它不会影响组件的长期输出功率和可靠性，这与其他的独立研究的发现相同。

So then, what causes snail trail? In a module, a polymer called ethylene vinyl acetate (EVA) encapsulates the cells. In order to determine the cause, Canadian Solar took the affected solar cell fragments with dark lines on the surface out of the modules and examined them under a high magnification scanning electron microscope - in order to examine them better and view their cross-section, the samples require cutting. The images reveal that the discolored material sits right at the interface between the silver fingers of the cells and the encapsulation polymer. There is no color/metallization structural change in the silver fingers, therefore the conductivity of the modules remained intact. The discolored layer appears on the surface above the metallization, and does not cast a shadow on the cell surface. The results from the examination prove that the crisscrossing dark lines have no direct negative influence on the module power output. Also conducted was an elemental analysis on the discolored regions in both the transverse and cross-sectional directions. Certain transition metal elements and their oxide aggregated at the dark regions comparing to the normal regions.

那么,是什么导致了蜗牛纹?在组件中，是用乙烯-醋酸乙烯聚物(EVA)封装电池。为了找到原因，阿特斯从组件中取出了表面受黑线影响的太阳能电池碎片，为了更好的观察，将其放置在高倍电子扫描显微镜下，并切割样品观察其横截面。获得的图像显示,变色部分正位于电池的银浆和封装聚合物的界面之间。银浆本身没有颜色/金属结构的变化,因此组件的导电率仍然完好。变色层出现在银浆表面正上方，所以电池表面不会有阴影。试验的结果证明交错的暗线对于输出功率没有直接的负面影响。在变色区域的横向和纵向做元素分析，并在变色区与正常区域分析比较某些过渡金属元素及其氧化聚合。

However, in order to understand, fully, the investigation, we have to recognize that snail trail is not a new phenomenon that popped up suddenly in the last few years. If you go through the literature database and peruse past articles regarding the encapsulation materials, you will find that it first appeared nearly three decades ago. In 1983, researchers noted that over the contact grid lines of cells, the EVA-based encapsulant turned dark brown. They also found that grid-line browning only happened over the finger grids, while areas over the ribbons remained shiny. The above descriptions coincide with that of snail trail perfectly. Based on their findings researchers, at the time, speculated that transition metal oxides in the grid line catalyzed the reactions in the EVA and caused the discoloration of the polymer just above the grid lines.

然而,为了充分理解此调查,我们需要知道,蜗牛纹不是近几年突然出现的新现象。如果你仔细查看关于封装材料的文献数据库并细读过去的文章,你会发现它的第一次出现是近30年前。1983年,研究人员发现, 接触电池栅线的EVA类封装材料变成了深棕色。他们还发现褐变的网格线只发生在栅线上,而焊带区域仍然有光泽。以上描述与蜗牛纹完全一致。基于以上发现，研究员当时就推测栅线上的过渡金属氧化物催化了EVA中发生的反应并带来栅线上聚合物的颜色变化。

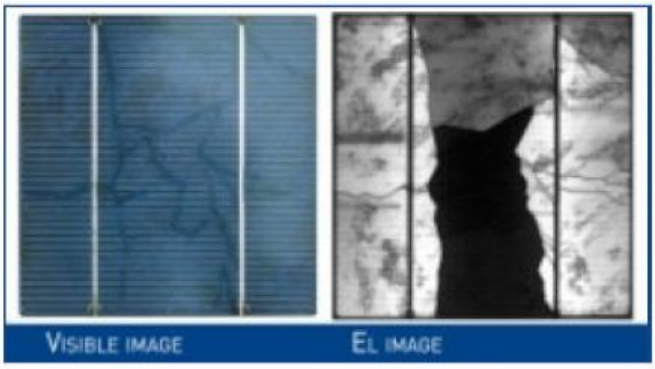
Following past research, Canadian Solar continued to investigate snail trail, and found that cells with certain types of silver pastes are more prone to snail trail than others. The production of solar cells is by printing silver paste on the top surface and then oven sintering them. The silver paste burns through the top anti-reflection layer to make electrical contact with the underlying silicon. Conventional silver paste contains glass frits to smooth the printing and sintering process. Inside glass frits is the addition of metal oxides, and certain metal oxides are highly suspected as the culprit initiating the discoloring reactions inside the EVA.

基于以往的研究,阿特斯继续调查蜗牛纹,并发现使用某些类型银浆的电池比其他类型的电池更易发生蜗牛纹。太阳能电池的生产是在其表面印刷银浆,然后高温烧结。银浆烧蚀表面减反层与底层硅实现电气接触。传统银浆含有熔玻璃体，用来保证印刷和烧结的过程平稳进行。熔玻璃体的内部添加金属氧化物,并且此类金属氧化物被高度怀疑为开启 EVA 内部变色反应的罪魁祸首。

The addition of various chemicals in EVA enhances the material properties and improves resistance to environmental impacts such as UV light and oxidization. Peroxide is used to crosslink EVA in the lamination process, rendering the polymer hard and strong even in hot conditions. A UV absorbing additive is included to absorb UV light, while the addition of antioxidants protects against oxidization and annihilate free chemical radicals. The UV absorber and antioxidants work in a cyclic

way, which means they can regenerate after capturing the UV photons and the free radicals. Therefore, their concentration does not decrease over time, ensuring longevity of the EVA polymer. With consumption of UV absorber or antioxidants, the EVA will age quicker.

EVA中需添加各种化学物质来增强材料性能,改善耐候性例如耐紫外光和氧化等。用过氧化物实现层压过程中EVA交联反应，使聚合物即使在热条件下仍可保持坚硬牢固的状态。紫外线吸收剂用来吸收紫外线,同时添加抗氧化剂使其免受氧化并消除化学自由基。紫外线吸收剂和抗氧化剂以循环可逆的方式工作,这意味着他们在捕获紫外光子和自由基后可以再生。因此,他们的浓度不随时间减少,确保EVA聚合物的寿命。随着紫外线吸收剂或抗氧化剂的消耗, EVA将老化的更快。



Canadian Solar's hypothesis of the chemical reactions are the following: the transition metal oxides in the glass frits of the silver paste, the peroxide cross linker, the UV absorber, and the antioxidants are all involved in the chemical reaction. The transition metal oxides help break down the antioxidants in certain environments. The disappearing of antioxidants makes the residual peroxide cross-linker react with the UV absorber, generating dark colored materials. To test the company's hypothesis, first there were changes to the concentration of additives in the EVA, and then there was experimentation of different levels of additives with cells of different types of silver pastes. The results bolstered Canadian Solar's hypothesis. Since metal oxide resides in the silver grid line, the reaction happens only over the grid lines and does not spread over time.

阿特斯就此过程化学反应做出以下假设:含银浆的熔玻璃体内的过渡金属氧化物、过氧化物交联剂、紫外线吸收剂和抗氧化剂都参与化学反应。过渡金属氧化物帮助分解某些环境中的抗氧化剂。抗氧化剂的消失使剩余过氧化交联剂与紫外线吸收剂发生反应,生成深色材料。为了验证此假设,首先改变EVA里添加剂的浓度,然后实验不同级别的添加剂用在不同银浆类型的电池上。实验结果正验证了阿特斯的假设。既然金属氧化物在栅线中, 反应只在栅线区域且不随时间的改变而蔓延。

In conclusion, snail trail is an old story happening again in a new age and it does not affect actual solar module performance. Canadian Solar has found evidence that the cause is the addition of certain additives in the glass frits of silver paste and additives in the EVA. After controlling the solar cells, i.e., controlling the silver paste, this phenomenon disappears. To avoid snail trail,

solar module manufacturers need to continue to study the type of silver paste used and materials within the encapsulation polymer.

总之，蜗牛纹是一个较老的现象，不影响组件的功率输出。阿特斯研究发现的证据表明蜗牛纹主要是由于银浆的玻璃体及EVA中的添加剂互相反应造成。通过更换对电池片及其银浆后此现象不在产生。为避免此类现象发生组件厂应该深入了解银浆的构成以及封装材料（EVA）的添加剂构成。

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