

BACKSHEET CHALKING – THEORETICAL BACKGROUND AND RELATION TO BACKSHEET CRACKING AND INSULATION FAILURES

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ABSTRACT: This paper assesses the phenomenon of PV backsheet chalking and its effect on solar module reliability. We review the current state of literature on the chalking effect in general and discuss the commonly accepted photocatalytic mechanism of polymer degradation in paints and coatings. We then apply this general knowledge to solar backsheets and discuss its relevance for solar modules reliability and performance, including the experience we have gained from investigations on field-exposed modules. After a physical and chemical analysis identifying the powder as titanium dioxide (TiO_2), the important factors for the occurrence of backsheet chalking are determined as (a) the type of polymer layers, (b) the polymer formulation, and (c) the amount and location of TiO_2 in the backsheet. Finally, two cases of field-aged modules exemplify different degradation pathways, that both originate from the same degradation mechanism. Although backsheet chalking can, in some cases, be an indication for further degradation, an analytical investigation of the backsheet is necessary to determine the actually associated risk.

Keywords: Backsheet, Degradation, Durability, Polymer film, PV materials, Reliability, Safety, TiO_2

1 INTRODUCTION

Backsheet chalking is a failure mode of field-exposed modules that has recently been reported more frequently. It is observable as a white powder on the outer backsheet layer, which can be removed by extensive wiping or washing with water. The phenomenon is often observed in conjunction with a rough, matte backsheet surface, which is prone to mold formation and often appears in context with other, more severe module failures – such as backsheet cracking between cells and along busbars, and in some cases complete insulation failures. Furthermore, it seems that some types of backsheet polymer composite combinations are particularly affected by this degradation path or show more severe consequences.



Figure 1: Finger with white powder from chalking backsheet

An in-depth evaluation and classification of this failure mode is therefore needed in order to assess the severity of backsheet chalking and allow estimation of the resulting long-term effects for different backsheet foils. In this paper, we discuss the suitability of backsheet chalking as an early warning sign, as has already been applied in the similar area of TiO_2 pigmented paints[1]. Further, we determine the necessary actions to estimate failure development in the case of appearing backsheet chalking in the field.

2 POWDER ANALYSIS

The white powder observed on chalking backsheets was removed from the backsheet either mechanically with a spatula or with adhesive tape and subsequently analyzed by scanning electron microscopy (SEM),

energy-dispersive X-ray spectroscopy (EDX) and Raman spectroscopy.

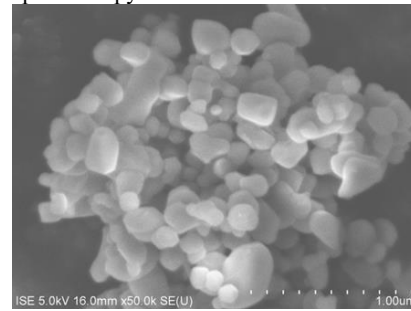


Figure 2: SEM image of chalking powder

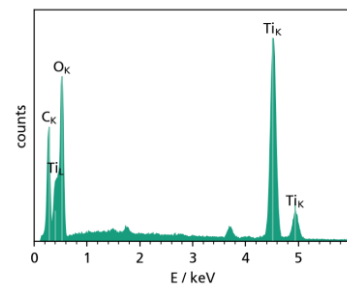


Figure 3: EDX spectrum of chalking powder

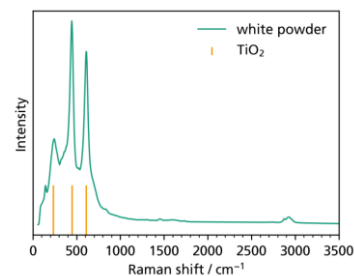


Figure 4: Raman spectrum of chalking powder

The SEM image (Figure 2) shows particles of a 100–400 nm in size, while the EDX (Figure 3) and Raman (Figure 4) identify the particles as titanium dioxide (titania, TiO_2): EDX shows the expected peaks

for titanium and oxygen atoms and the signals in the Raman spectrum correspond to TiO_2 rutile phonons. The latter method is also very useful for identifying the organic polymer and presence of TiO_2 of individual backsheet layers, as performed in our lab in conjunction with fourier-transformed infrared spectroscopy (FTIR, not shown).

3 THEORETICAL BACKGROUND: TiO_2 'S ROLE AS PIGMENT AND PHOTOCATALYST

TiO_2 pigment particles are added to the backsheet formulation in order to protect it from UV light. TiO_2 is by far the most commonly used inorganic pigment in coatings and paints due to its chemical stability and inertia, non-toxicity, and high refractive index[2]. The chalking phenomenon of TiO_2 has been known since the 1940s in the context of pigmented paints and coatings and could be linked to the photochemical properties of TiO_2 [3].

In order to avoid pigment agglomeration and improve the dispersion of TiO_2 in the polymer matrix of the backsheet, pigments are often coated with a thin layer of inorganic oxides such as alumina or silica and used in combination with an organic dispersant[2]. A good dispersion of TiO_2 pigments in the backsheet provides an optimal particle size to efficiently protect the backsheet by reflection of light, or, to a smaller extent, conversion to heat.

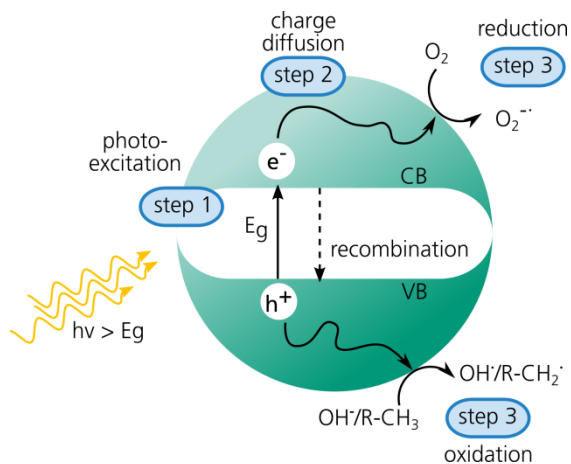


Figure 5: Photocatalysis mechanism at a TiO_2 particle

However, as a semiconductor, TiO_2 can also absorb light and initiate a photocatalytic process (Figure 5), which aggravates the degradation that is caused by UV light [4]: If the energy of incoming photons is larger than the band gap, electrons can be elevated across the band gap and electron hole pairs are created (step 1). In a second step, these charge carriers can be separated and subsequently diffuse to the particle surface if they don't recombine into a lower energy state, e.g., at bulk defects. At the surface, electrons and holes can perform reduction and oxidation reactions, respectively, and thereby form radical species (step 3): Reduction of oxygen (O_2) leads to the formation of the reactive superoxide radical ($\text{O}_2^{\bullet-}$), while holes can produce either hydroxyl radicals or form reactive alkyl species by directly abstracting hydrogen atoms from organic molecules, such as the polymer binder or the surrounding polymer matrix of the backsheet.

In any case, the formed radicals accelerate the degradation of the polymeric dispersant and the surrounding polymer. This degradation on the backsheet surface then leads to a detachment of pigment particles from the foil and to the observed chalking effect. The exact properties of TiO_2 pigments thereby have a strong effect on the extent of observed chalking, and are affected by the particle size, crystal structure (rutile/anatase ratio), amount and location (surface or bulk) of defects, TiO_2 surface functionalization, and coverage with inorganic oxides.

It is important to note that both chalking and photocatalysis are not exclusive properties of titania: Chalking has also been observed on polymer films with manganese oxide[5], and other, less common white pigments also exhibit photocatalytic activity, albeit to a smaller extent. A replacement of TiO_2 with an alternative pigment would therefore not necessarily avoid the chalking effect, but instead require the use of a higher pigment concentration in order to match TiO_2 's shielding abilities.

3.1 Effects of chalking in solar backsheets

In principle, all polymer types can exhibit some degree of backsheet chalking. Even the well-trying and tested combination of a PET core and PVF protecting layers, such as TPT, can be affected, as could be reproduced in the lab by combined UV damp-heat aging 190 kWh/m^2 , 85°C , $85\% \text{ r. h.}$, 1000 h [6].

However, the severity of failures linked to backsheet chalking, such as backsheet cracking and insulation failures, are strongly dependent on (a) the kind of polymer layers included in the backsheet composite, (b) the polymer formulation and addition of stabilizers, and (c) the amount and location (*i.e.* which layer) of TiO_2 pigments present in the backsheet.

Concerning the polymer material (a), the increase in reported cases of backsheet chalking with severe module failures seems to correlate with the increased use of alternative polymers, in contrast to the conventional combination of PET core layer and fluoropolymer outer and inner layer. Indeed, we have no knowledge of a report of a module failure in which pigment chalking of such a backsheet type could be proven to be the root cause.

On the other hand, there are also many examples of backsheets consisting of "new" polyamide (PA) or polyolefin layers as main polymer components which perform reliably in various outdoor scenarios. Some of these newly developed materials are even more durable than their conventional counterparts[6]. It therefore seems that (b) the exact production parameters and formulation of the polymer, *i.e.* the addition of stabilizers against the effects of UV irradiation, temperature, moisture, and diffusing gases has a large impact on the durability of the backsheet. The right combination and quantities of these components – which have to be determined in extensive reliability tests during the development phase – might be harder to optimize for some polymer materials than for others, which could explain the recent increase in occurrence of backsheet-related module failures.

As mentioned in (c), the use of TiO_2 in different backsheet layers can result in differences of degradation, as illustrated in Figure 6. Most commonly, TiO_2 pigments are used in the outer backsheet protection layer as UV blocker (Figure 6, left). In this case the discussed

photocatalysis mechanism can substantially damage the respective layer, via the produced radicals, and release TiO_2 particles, which are then observed as chalking powder. This process does not in itself affect module safety or performance directly; in the long run, however, this can initiate a cascade of further degradation: Without proper protection by the outer backsheet layer, UV light and moisture reach the core backsheet layer, which directly reduces the electric insulation and safety of the module. Furthermore, moisture can diffuse further into the modules and lead to corrosion of cells and connectors, which has a negative impact on module performance.

In some cases, TiO_2 pigments reside in a layer inside the backsheet sandwich, e.g. core- (Figure 6, right) or inner/adhesion layer. In principle, this can lead to a very similar degradation behavior and damage the layer that comprises the pigments, with the difference that TiO_2 particles are constrained inside the backsheet and no chalking is observed on the outside. Possible further degradation pathways are independent of the exact pigment location. This case is therefore usually detected only after further degradation occurs, e.g. loss of adhesion with the consequence of low insulation properties or cracking of the backsheet.

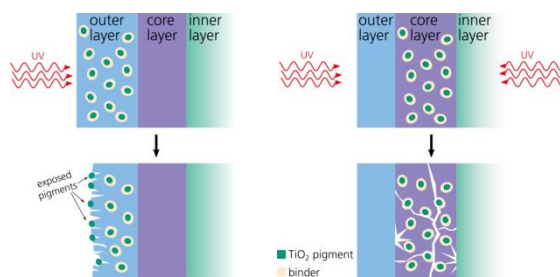


Figure 6: Photocatalytic effect of TiO_2 pigments in the outer (left) and core (right) backsheet layer

4 BACKSHEET CHALKING ON FIELD-EXPOSED MODULES

4.1 Exemplary cases of field-aged modules

In general, weak chalking does not necessarily lead to the severe module degradation modes discussed above; we believe that certain module types affected by backsheet chalking could function without further problems throughout the expected lifetime, although this would be difficult to verify with certainty in a lab.

Backsheet chalking can, however, be an early indication of future degradation. As an example, the microscope analysis of a chalking backsheet cross section shows cracks in the outer PA protection layer, which contains TiO_2 (Figure 7). Although the respective modules showed no other peculiarities in the field, further degradation, including lowered insulation properties and reduced power output, is very likely as discussed above and already indicated by a weak adhesion between the inner PET and PA backsheets layers, leading to delamination. In this case, crack formation could also be observed in the inner PA layer, which also contains TiO_2 .

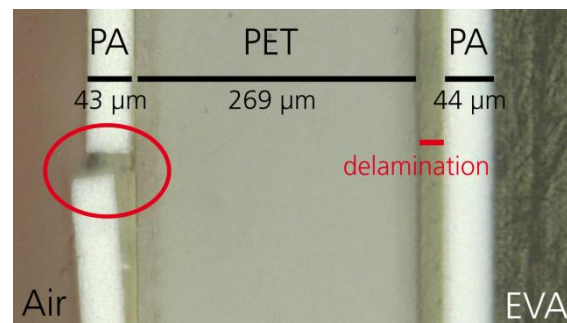


Figure 7: Microscopic image of a cross-section of a backsheet that exhibits chalking shows a crack in the outer protection layer. Both white PA layers contain TiO_2

In another case of field-aged modules, severe drops in insulation properties were observed, in some cases leading to complete failure of modules. A microscopic analysis of the backsheet cross-section of modules with low insulation revealed a severely damaged, TiO_2 -containing PP layer (Figure 8, right). This is an example for the same photocatalytic mechanism (Figure 6, right) that does not lead to a visible chalking effect because the TiO_2 particles are still confined inside the backsheet sandwich. The resulting cohesion loss of the white PP layer was observed across the whole module.

Another module from the same type and outdoor site with decent insulation values was analyzed in the same way. The respective backsheet was intact at locations that were covered from front irradiation by solar cells. Between the cells, however, it was also strongly damaged. We conclude that these modules only represent an earlier state of degradation, e.g., due to slightly different exposure parameters in the field, and that the degradation will continue, going down the path of the more damaged modules.

This is another example of TiO_2 -related module degradation, in which the analysis of the backsheet can reveal a module failure before other severe effects are observed.

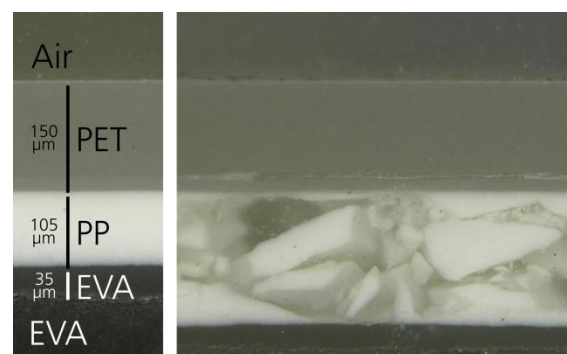


Figure 8: Microscopic image of intact (left) and damaged (right) backsheet cross section. The scale is the same for both images

5 CONCLUSION

In the recent past an increasing number of chalking backsheet findings has coincided with severe cracks of the backsheet and insulation losses. At the same time, we also see an increase of cases with weak insulation without the occurrence of backsheet chalking.

As discussed above, backsheet chalking can, in some cases, be an indication for backsheet cracks and provide

an early warning for further degradation. But the exact course of further development depends on various properties of the backsheet. With knowledge of the underlying degradation mechanism, an analytical investigation of the backsheet can help understanding the actually associated risk and future development.

6 EXPERIMENTAL

Cross-sectional samples were prepared by cutting pieces of the backsheet and EVA from locations of interest from the module. These polymer laminates were then embedded in epoxy resin and afterwards ground and polished in order to reveal a flat and even surface at the location of interest. The thickness of individual polymer layers was measured with an optical microscope. The values given in the microscope images are averages of 10 individual measurements.

Electron microscopy and energy-dispersive X-ray spectroscopy (EDX) measurements were carried out using an Environmental Scanning Electron Microscope ESEM (FEI Quanta 400) with integrated EDX spectroscopy system (EDAX Genesis) at an acceleration voltage of 10 kV.

The Raman spectroscopic measurements were performed using a WiTec Alpha 500 Raman microscope with a 532 nm laser, which is obtained using a frequency doubled Nd:YAG laser with a maximum excitation power of around 17 mW. The CCD detector was thermoelectrically cooled to -67 °C.

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