Solar Energy Materials & Solar Cells 93 (2009) 630–640

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Adhesion and thermal stability of thickness insensitive spectrally selective (TISS) polyurethane-based paint coatings on copper substrates

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ARTICLE INFO

Article history:
Received 9 October 2008
Accepted 18 December 2008
Available online 25 January 2009

Keywords:
Accelerated test procedure
Lifetime assessment
Spectral selectivity
Organic coatings
Solar absorbers

ABSTRACT

Thickness insensitive spectrally selective (TISS) paint coatings based on a polyurethane polymeric binder deposited on copper substrates were investigated to obtain information about their service lifetime. The degradation of TISS paint coatings was performed according to the methodology worked out within Task 10 of the IEA's Solar heating and the cooling programme. The activation energy (E_a) for the degradation process was derived from vibrational band changes of the polyurethane binder recorded in the infrared hemispherical reflectance spectra of TISS paint coatings exposed to different thermal loads. The results of the vibrational band analysis were correlated with cross-cut tests, showing that the coatings started to lose integrity at 190 °C but protected the copper substrate against oxidation perfectly even at 200 °C (15 days). An accelerated test procedure confirmed that TISS coatings could be safely used in solar collectors for at least 45 years.

1. Introduction

Due to increasing demands to substitute fossil fuel heating in Europe by buildings with heat obtained from solar collector systems, the assessment of the service lifetime and the related failure time of solar absorber coatings is an area of growing interest. This follows naturally from the relevance of the long-term stability of solar absorber coatings to the solar radiation-to-heat conversion efficiency. The problem is not trivial since it requires, among many other factors, a detailed knowledge of various solar collector systems, assessment of how various loads affect their performance and an understanding of optical properties in relation to the structural changes, that accompany degradation during the service time [1–5].

In the last decade, extensive theoretical work supported and substantiated by the degradation assessment of absorbers in the field has been performed, based on the methodology worked out within IEA-SHC Task 10 [6]. This work lead to a recommended accelerated test procedure [7–9], enabling predictions of the suitability of solar absorber coatings for use in single glazed flat plate collectors for domestic hot water systems. The essential part of this procedure is the establishment of various load (thermal, mechanical and humidity) tests performed in the laboratory, together with the performance criterion for their 'suitability'. The latter issue was extensively discussed and this resulted in the performance criterion (PC) function, which states that during the service life of 25 years, the system should not show a loss of the solar fraction greater than 5%. The existing accelerated tests include possible causes of degradation such as high thermal load, condensation, humidity and atmospheric corrosion by SO_2. The outcome of accelerated tests is the failure time expressed in years when the PC of the coatings exceeds the 5% limit.

The recommended accelerated test procedure has been verified for many inorganic coatings such as Black Chrome, Sunselect, Mirotherm and some other of the PVD/CVD cermet coatings [10,11] nowadays most commonly used worldwide, and their service lifetime have already been predicted. However, for the thickness insensitive spectrally selective (TISS) paint coatings recently developed in our laboratory [12–14], which are based on pigments embedded in organic resin binders, the accelerated test procedure methodology has not yet been examined. Accordingly, in this study we focused on verification of the suitability of the existing accelerated test procedure for the service lifetime prediction for TISS paint coatings, also with the aim of pointing out some problems specific for the assessment of the failure time of organic coatings in general.

The main problem encountered while applying the recommended accelerated test procedure for TISS paint coatings was firstly, the selection and application of suitable thermal loads, and secondly, combining the observed degradation inferred from

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0927-0248/$ - see front matter © 2009 Published by Elsevier B.V.
doi:10.1016/j.solmat.2008.12.026

spectral selectivity changes with suitable additional indicators, which reflected the coatings' integrity (cohesion) and adhesion onto the copper substrate. According to the recommended accelerated test procedure, the coatings should be exposed for shorter time intervals (up to a few weeks) to temperatures close to and above 230 °C [8,11], depending on the stagnation temperature of the solar collector. Such thermal loads exceed the thermal stability of the polyurethane resin binder, which was used for making TISS paint coatings, also permitting the oxidation of the copper substrate (i.e. formation of Cu_2O) [15].

For prediction of the service lifetime, it is necessary to know the activation energy (E_a) (Arrhenius law) attributed to the specific degradation process of TISS paint coatings taking place in the course of the accelerated tests. In general, the activation energy can be determined from the measured changes of any of the material properties, which could serve as a degradation indicator [16]. In the case of inorganic absorber coatings, it was found that thermal emittance and solar absorptance values derived from the measured reflectance spectra are a good choice. However, TISS paint coatings are specific and in certain aspects quite complex systems for which the solar absorptance and thermal emittance values depend on various factors. These include binder decomposition, causing formation of pores with the ingression of oxygen leading to oxidation of the copper substrate (i.e. Cu_2O) and the changes in paint morphology due to reorientation and collapse of large aluminium pigment flakes. In fact, it was observed that high-temperature treatment of TISS paint coatings leads to an increase of the absorptance and a decrease in the emittance—which is not degradation in the sense of worsening the performance of a solar thermal system.

Adhesion tests performed on TISS paint coatings during tempering suggest that the loss in adhesion/cohesion, which is a consequence of the decomposition of the binder, is the appropriate failure mode for determining the lifetime of this kind of absorber. Thus, for obtaining the activation energy attributed to the degradation of TISS paint coatings in this study, the integral intensity changes exhibited by selected vibrational bands of the resin binder observed in the reflectance spectra of TISS paint coatings were used. By taking into account the vibrational bands of the binder as a measure for the paint's degradation, we excluded other effects such as densification and morphological changes of the paint coatings, causing unexpected shifts in the reflectance curves, which may interfere with the expected complex degradation processes of TISS paint coatings. In the final step, the failure time of TISS coatings was assessed from the determined activation energy by taking into account the results of cross-cut tests performed on TISS coatings exposed to the same thermal loads. Cross-cut tests represented the additional criteria which were included in the failure time assessment presented in this work.

2. Experimental

2.1. Instrumental

The optical properties of paint coatings were determined from infrared (IR) reflectance spectra. Reflectance spectra in the visible (VIS) and near-infrared (NIR) range were measured on a Perkin Elmer Lambda 950 UV/Vis/NIR with an integrating sphere (modul 150 mm), while reflectance spectra in the middle IR spectral range were obtained on a Bruker IFS 66/S spectrometer, equipped with an integrating sphere (OPTOSOL), using a gold plate as a standard for diffuse reflectance. Solar absorptance (a_s) and thermal emittance (e_T) values were determined from the reflectance spectra using a standard procedure [17], as reported previously [12,13].

2.2. Preparation of TISS paints

TISS paints were prepared using a standard procedure [12,13]. Black ($CuCr_2O_4$ spinel black (Ferro, D)) pigment dispersions were prepared first, by mixing the corresponding pigment with the

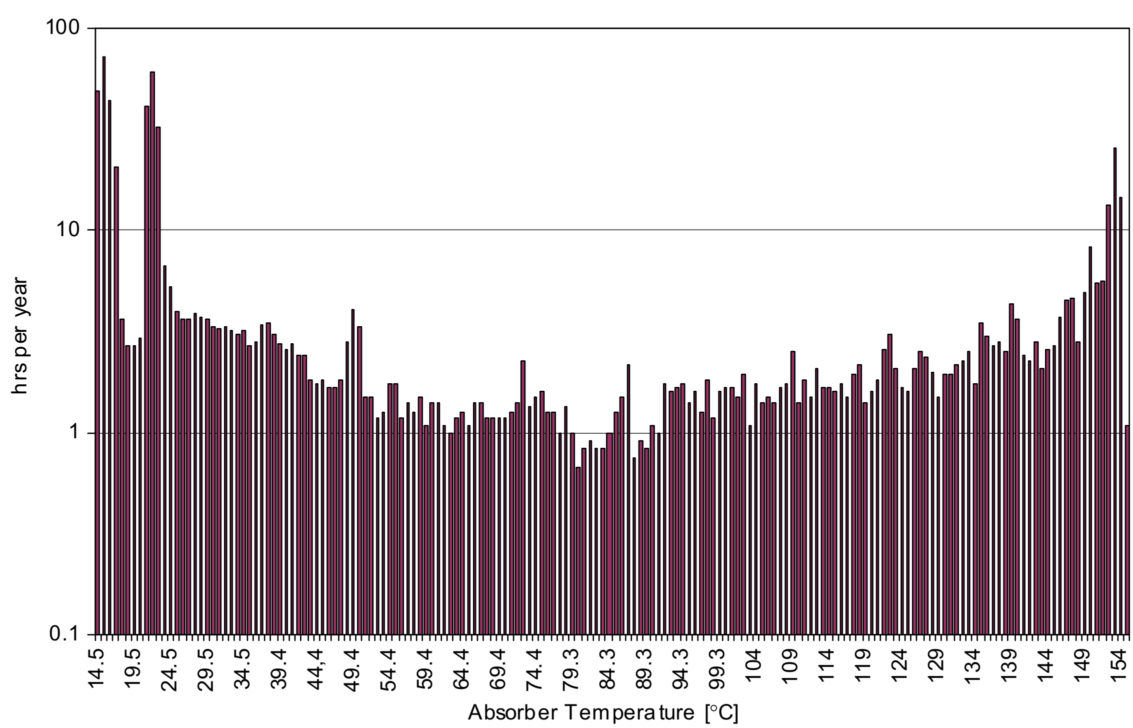

Fig. 1. Transposed histogram of the stagnation temperature T_{st} expressed in hours/per year for a solar absorber with TISS paint coating having a_s ~0.90, e_T ~0.40 and T_{st} ~155 °C.