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Bachelor of Science in Materials Engineering

Effect of Thermal ageing on two selective paint coatings based on polysiloxane and polyurethane

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2 ABSTRACT

Solar thermal collectors are a low cost and eco-friendly alternative for energy production. The essential component in the collector is the solar absorber since it is where the photo-thermal conversion occurs. One of the factors that change the absorber's effectiveness is the type of coating used. In this dissertation, spectrally selective paint coatings are studied – PC2 based on silicone and PC3 based on polyurethane. The degradation of both paints when subjected to temperature accelerated ageing tests is studied. Tests were carried out at 320°C for 300 and 600 hours. The fixed vehicle of the paints was analysed by FTIR. The *spectra* of the composition of the paints before and after the ageing test were analysed by FTIR-ATR. In PC2 there was no change in the spectrum after ageing; however, in PC3 there was a change in the structure of the paint, which lost polymer after ageing. Thermogravimetric tests were carried out in an inert and oxidative atmosphere. In PC2 a low percentage of mass loss was identified while in PC3 the percentage of mass loss was more accentuated, thus verifying both FTIR-ATR results. To complete the analysis, the samples were analysed in a SEM/EDS. Finally, these results were compared with the optical properties of the paint, concluding that although the optical properties of both paints behave similarly after the ageing test, spectrally selective paints, depending on their composition, have distinct degradation behaviours when subjected to high temperatures.

3 RESUMO

Os coletores solares térmicos são uma alternativa de baixo custo e amiga do ambiente para a produção de energia. O componente fundamental no coletor é o absorsor, visto que é neste que se realiza a conversão foto-térmica. Um dos fatores que modifica a eficácia do absorsor é o tipo de revestimento utilizado. Nesta dissertação são estudados revestimentos de tintas espectralmente seletivas – PC2 de base silicone e PC3 de base poliuretano. Na presente dissertação é estudada a degradação de ambas as tintas quando sujeitas a ensaios de envelhecimento acelerado por temperatura. Foram realizados ensaios a 320°C por 300 e 600 horas. O veículo fixo das tintas foi analisado por FTIR. Os espectros da composição das tintas antes e depois do ensaio de envelhecimento foram adquiridos em FTIR-ATR. No PC2 não se verificou alterações no espectro após envelhecimento; no entanto, no PC3 existiu uma alteração na estrutura da tinta tendo esta perdido polímero após o envelhecimento. Foram realizados ensaios de termogravimetria em atmosfera inerte e oxidativa. No PC2 foi identificada uma baixa confirmando os resultados obtidos em FTIR-ATR. Para completar a análise, as amostras foram analisadas por SEM/EDS. Por fim, estes resultados foram comparados com as propriedades óticas das tintas, concluindo que apesar das propriedades óticas de ambas as tintas terem um comportamento semelhante após o ensaio de envelhecimento, as tintas espectralmente selectivas, dependedo da sua composição, têm comportamentos de degradação distintos, quando sujeitas a temperaturas elevadas.

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7 ACRONYMS

LNEG Laboratório Nacional de Energia e Geologia.

LMR Laboratório de Materiais e Revestimentos.

LES Laboratório de Energia Solar.

CENIMAT Centro de Investigação de Materiais.

STC Solar Thermal Collector.

FPC Flat Plate collector.

PVC Pigment Volume Concentration

PVD Physical Vapour Deposition.

CVD Evaporation Vapour Deposition.

TSSS Thickness Sensitive Spectrally Selective.

TISS Thickness Insensitive Spectrally Selective.

PC2 SUNCOLOR TS S Black and SOLKOTE HI/SORB-II ™

PC3 SUNCOLOR PUR Black

FT-IR Fourier Transform Infrared Spectroscopy.

IR Infrared Radiation

ATR Attenuated Total Reflectance.

TGA Thermogravimetric Analysis.

SEM Scanning Electron Microscope.

SE Secondary Electron.

BSE Backscattered Electron.

EDS Energy Dispersive Spectroscopy.

8 OBJECTIVES AND MOTIVATION

As we live in a world that is increasingly alert to the problems of global warming, we are forced to find solutions for reducing greenhouse gases sent into the atmosphere. The use of renewable energies is increasingly generalized as a source of energy production. Solar thermal collectors are an eco-friendly solution for energy production. However, because they are exposed to different environmental factors, they suffer degradation that can affect the long-term efficiency of the collector.

The aim of this thesis is the evaluation of the changes of optical properties, composition and morphology of two absorbers based on two different selective coatings – one with polysiloxane binder and the other with polyurethane binder. Therefore, it was intended to carry out accelerated ageing tests where the samples are subjected to a 320°C for a certain period of time. After these tests, the structures of the initial samples and aged samples are analysed and compared. The final objective of this thesis is envisaging the application of these two coatings in systems operating at higher temperatures.

The objectives of this master's thesis are:

- Identifying the chemical changes in solar absorber coatings, based on spectrally selective paints, after exposure to temperature
- Relating these changes with the changes in their optical properties

All steps were performed at Laboratório Nacional de Energia e Geologia (LNEG) – Laboratório de Materiais e Revestimentos (LMR), Laboratório de Energia Solar (LES) e Unidade de Bioenergia e Biorefinarias (UBB) and at CENIMAT/I3N.

10 INTRODUCTION

10.1 SOLAR THERMAL COLLECTORS:

Solar thermal collectors (STCs) are an eco-friendly way of gathering energy. Using solar energy it is possible to avoid releasing greenhouse gases into the atmosphere [1]. STCs are the main component of thermal systems for production of hot water at home (range of use 20-95°C) and for industrial applications (range of use 95-250 °C) [2].

Flat plate collectors (FPCs), an example of solar thermal collectors, are used for low temperature applications [2], usually in a fixed position, and therefore need to be oriented appropriately. The collectors for low temperature applications must withstand conditions such as high temperatures, high humidity, ultraviolet irradiance [3], wind, snow and atmospheric corrosivity [4]. Figure 1 shows a schematic representation of a solar thermal collector.
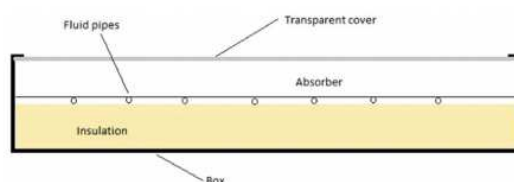
Figure 1-Representation of a solar flat plate collector. [2]

STCs are composed of a frame (box) usually metallic (polymeric materials can be used to develop lower cost solutions) with several elements. An insulation is used in the backside of the absorber to avoid or reduce thermal losses to the environment [2]. It is usually made of rock wool or glass wool due to its low thermal conductivity and high thermal resistance. The most important part of an STCs is the absorber. Absorbers are usually made of a metallic substrate (copper or aluminium with 0.2-0.5 mm thickness) with a coating (organic or inorganic) and are used to absorb incident solar radiation [2]. For low temperature heating (such as swimming pools) the absorber can be made exclusively of polymeric materials to lower the cost. The absorber is connected to a grid of pipes, the risers, made of copper (due to its high conductivity and corrosion resistance). This grid being projected for circulation of the heat transfer fluid (water, water/glycol mixture, where glycol is used as antifreeze to protect the collectors from freezing), which must have high thermal conductivity, low viscosity and toxicity, and low cost. The connection between the absorber and the risers is usually carried out by welding processes [5].

A transparent cover is applied in the front of the absorber. The cover must have high transmittance (in the range of solar radiation) because only the irradiance reaching the absorber can be used for photo-thermal conversion. Low iron glass is often the chosen material due to is transparent behaviour to solar radiation (shortwave radiation 300 nm to 2500 nm) and opaque behaviour to longwave radiation (2.5-40 μm). This means that low iron glass has high transmissivity of shortwave radiation and low transmissivity of longwave radiation [2, 5, 6].

Incident solar radiation with a wavelength of 300 < λ < 2500 nm shines onto the transparent cover and approximately 90% of this radiation is transmitted through the cover (8%

of the incident solar radiation is lost due to reflection and 2% of that radiation is absorbed by the transparent cover), which can be used for the photo-thermal conversion [5].

The absorber has a crucial role in the photo-thermal conversion on account of the absorptance of the absorber coating, as will be discussed in the following section. Higher absorptivity leads to more solar radiation converted into heat. Typical values of the absorptivity are approximately 93%. That means that just 7% of the incoming solar radiation is reflected [5].

Figure 2 exemplifies the physical processes that take place within the solar thermal collector.
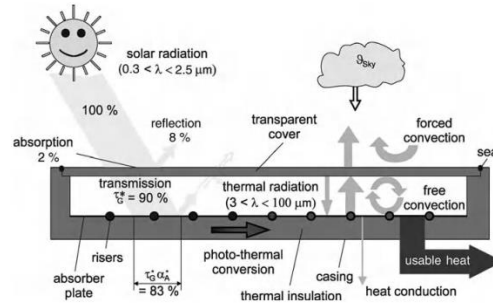
Figure 2 - Physical processes inside the solar thermal collector [5].

The absorber is heated up by the absorbed solar radiation resulting in a temperature difference between the absorber and the transparent cover. As a result of the temperature difference, free convection is developed leading to heat transfer from the hot surface of the absorber to the cold transparent cover. This and the radiation heat transfer lead to a rise in the temperature of the transparent cover. Due to this, free convection is created on the outside of the transparent cover, leading to heat losses to the environment. These losses can be increased by significant wind speeds, leading to an additional forced convection [5].

In the risers, the heat transfer fluid is flowing with lower temperature compared with the absorber temperature. Thermal conduction is used to transfer heat from the hot absorber to the risers; thermal convection is used to transfer heat from the inside surface of the riser pipes to the heat transfer fluid [5].

Every device emits heat according to its temperature and emissivity. For a flat plate solar thermal collector, the wavelength of the emitted heat radiation is $3 < \lambda < 100$ µm. The radiation heat transfer occurs between the absorber and the transparent cover and the transparent cover with the sky [5].

During the development of solar thermal collectors it is important not only to enhance thermal performance but also to increase reliability and long-term performance stability [2]. Thermal performance depends, among other factors, on the transmittance of the transparent cover, the absorption and thermal emittance of the absorber, the conduction of solar energy and good conductivity of the working fluid [7]. Eq. 1 presents the energetic balance of the solar thermal collector.

$$Q_u = Q_{abs} - Q_{loss} \qquad \text{(Eq. 1)}$$

where Q_u is the useful energy delivered by the collector in the form of temperature increment of the heat transfer fluid, Q_{abs} is the energy absorbed resulting from the conversion of solar radiation incident on the absorber to thermal energy (heat), which depends on radiation absorptance and on the coefficient of transmission of the collector cover (τ), and Q_{loss} is the energy lost to the environment by conduction, convection and radiation losses and it is dependent on the thermal emittance of the absorber coating, on the thermal properties of insulation and on the distance between the absorber and the glass [2].

10.2 Spectrally Selective absorber coatings:

The solar selective absorber coatings have excellent features for applications related to solar photo-thermal conversion. Such coatings simultaneously possess high solar absorptivity (in the wavelength range of 300–2500 nm) and low thermal emissivity in the infrared region [8].

Solar absorptance (α_s) and thermal emittance (ε_t) are the optical properties of the absorber coating that have a major impact in the collector efficiency [2]. The optical performance (thermal emittance and solar absorptance) of the coating depends on: pigment, particle size, binder, thickness and solar absorptance gradient [9], as explained further. These surfaces have high absorptance, absorbing nearly 100% of the short wavelength radiation [5]. Additionally, they should have low emittance, in order not to lose much of the thermal energy through re-radiation from the heated surface [4].

10.3 Spectrally selective coatings produced by PVD processes:

In the past, black paint or black chromium were used as the main materials for selective coatings. During the last years, selective coating processes based on physical vapour deposition (PVD) have been more frequently developed, compared with other techniques, such as evaporation vapour deposition (CVD), and sputtering. The simplicity and low cost of solution-based processing allows it to be a possible candidate for large-scale deposition of spectrally selective coatings. These coatings improved the performance of the collector. Having a selective structure on the surface of the absorber instead of black paint generally improves the absorption by 5% and can decrease the emission by 60%, improving the optical properties and consequently the efficiency of the collector [5].

PVD is used for a large area deposition of thin films and has a relatively high deposition rate, reproducibility and precise control in thickness and deposition parameters [1]. However, coatings produced with PVD processes have some disadvantages such as low durability, low resistance to corrosion and to abrasion, high cost and complex production techniques [2].

10.4 Spectrally selective paints:

Nowadays, spectrally selective paints are a potential alternative for the absorbing surface. These coatings exhibit attractive features such as: ease of processing, low cost, applicability to numerous substrates (steel, copper, aluminium, or polymer), ease of field maintenance and durability. There are a few paints available that show high absorptance and low emittance [1, 2].

Generally, paint is made of binders, pigments, extenders, solvents and additives. Paint can be defined as pigment and extender particles evenly distributed (dispersed) in a resin binder (nearly always organic), with additives and solvents [2, 9].

The binder ensures the adhesion of the paint to the substrate and can be classified by its curing process. If the cure is done with solvent evaporation it is called thermoplastic; if the cure occurs by chemical reaction it is thermosetting [2, 11]. The solvent is the volatile vehicle of

the paint and one of the functions of the solvent is to dissolve the binder in order to decrease the paint's viscosity. Viscosity is an important factor that depends on the molecular weight of the resin and its dilution in the solvent. Higher molecular weight leads to a higher viscosity. In paints, it is desirable to have low viscosity to be able to apply it on the surface. However, the viscosity needs to be high enough not to drip [11].

Pigments are solid particles (nearly insoluble) that ensure the opacity and colour of paints. Extenders are substances that are insoluble in the application medium and are used to adjust the properties of a coating, to increase volume and to obtain technical properties. Finally, additives are used to improve paint properties and prevent film defects, being classified according to their function [11]. Of all additives that can be used, dispersants are some of the most important [2, 9].

There are two types of spectrally selective paints: "Thickness Insensitive Spectrally Selective" (TISS) paints and "Thickness Sensitive Spectrally Selective" (TSSS) paints. Both these types of paints feature the same basic principles regarding their composition and application.

When the concept of spectral selectivity was introduced in the solar absorber area, it was based on the absorber-reflector tandem technique. In this technique, selectivity is achieved through successive deposition of highly reflecting and solar absorbing materials in substrates with low emittance (such as aluminium or copper) [5]. The combination of high solar absorptance of paint coatings combined with low thermal emittance of metal absorbers results in high efficiency of the solar collector [12].

Optical properties of a TSSS paint depend on paint thickness. In order to achieve high absorptance ($\alpha_s \approx 0.90$) and low emittance ($\varepsilon_t = 0.25 - 0.3$) in TSSS paints the paint layer thickness should have values between 1 and 2 μm. Their spectral selectivity depends on the thermal emittance of the metal substrate, as explained in the absorber-reflector tandem. This limits the use of mild steel protected with corrosion resistance alloys (zinc, Zn and aluminium, Al) in unglazed facade solar thermal systems. However, the main limitation, for application of TSSS in facade absorbers, is the fact that TSSS paints are usually black or dark blue. For all these reasons, TSSS paint is used in glazed solar thermal systems [13]. For applications such as unglazed facade solar thermal systems (in which aesthetic criteria is important [2]), TISS paints are used because its optical properties do not depend on the paint thickness. TISS paint can be applied onto metal and non-metal surfaces, can be used in many colours and exhibit spectrally selectivity ($\alpha_s \approx 0.84 - 90$ and $\varepsilon_t = 0.31 - 0.41$ [14]) [12, 14]. Low thermal emittance of black and coloured versions of TISS paint coatings is provided by the addition of metallic flake pigment (for example, aluminium or copper), that take over the role of the low-emitting metal substrate in TSSS coatings [14].

Pigments used for preparation of TSSS paint must possess good covering efficiency, which for black pigments is easily achievable, and transparency of the paint layer in the infrared region. Lower/better emittance was achieved when the pigment with higher reflectivity was used in the preparation of the paint. Different shades of pigments influence the absorption and scattering in the visible and near-infrared spectral region. Studies show that unfortunately, the measured solar absorptance is high (< 0.9) only for black paints. Even for thicker paint layers (> 3g/m^2) the absorptance for pure green coatings was about 0.8 with corresponding emittance higher than 0.6 and low selectivity (a$_s$/e$_t$) of the green paint is a consequence of very low a$_s$ of the green pigment [16]. To obtain low emittance only thin layers of the paint must be applied. The pigments used in TISS and TSSS paint coatings should not have less than 200 nm. This limit needs to be respected because grinding the pigments to a smaller size results in unwanted changes in colour, reduction of the concealment power of the coating and increase in

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transparency. The consequence of these changes is a higher consumption of pigment to achieve the desired solar absorptance [5].

The resin must be strongly infrared absorbing because otherwise, increasing the pigment volume concentration (PVC) ratio can decrease the infrared transmittance of the paint film. However, high PVC ratio decreases the resistance of the paint film to abrasion. This leads to an increase in the surface roughness of the paint, which on the other hand beneficially affects the a_s value of the paint by decreasing reflection losses [17]. To make TISS or TSSS paint coatings different types of resin binders can be used, such as silicone and polyurethane binders. The binder must be firmly anchored onto the pigment surface. To achieve this anchorage, a thin layer of dispersant firmly attached to the surface of the pigment is used, to assure the compatibility of the pigment particle with the resin binder system. Dispersant can change pigment surface from hydrophilic to organophilic [5, 15].

In the case of spectrally selective coatings, a thin and homogeneous layer of paint is desired. For that reason, the pigment particles must be arranged into a well-defined layer, without excessive parts at which no pigments cover the substrate [5]. Figure 4 represents an ill-defined layer.
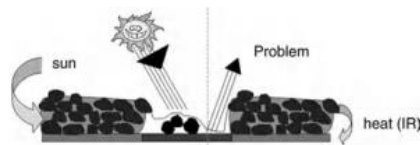
Figure 3 - Schematic presentation of TSSS paint coatings with non-evenly distributed pigment, stemming from agglomerated pigment particles [5].

Solar absorber surfaces are prone to degradation/ageing along the lifetime of the solar thermal collector. Temperature of operation and environmental parameters such as humidity, pollutants and chloride ions may result in the decrease of their optical performance [1].

10.5 DURABILITY OF SOLAR ABSORBER SURFACES

10.5.1 Ageing tests

Natural exposure tests carried out in environments similar to those where the equipments will operate are the most reliable way to know the changes of the materials properties upon ageing. But these tests are in general lengthy and it can take years to get information about materials degradation.

Accelerated ageing tests, in which the stress levels of one or more degradation factors are kept higher relative to in-use conditions, allow obtaining information about materials degradation in shorter periods. These tests consist of placing samples in artificial environments (in climatic chambers) where they are subjected to known conditions and to the atmospheric agents that most affect the corrosive process such as temperature, humidity, irradiance and pollutants (SO_2 and NO_2).

For solar absorber surfaces a set of accelerated tests, specified in the standard ISO 22975-3:2014 [19] was developed in order to guarantee a lifetime of at least 25 years. In this standard, the effects of temperature, resistance to condensed water and resistance to high humidity air containing SO_2 are considered, and a performance criterion for qualification of the

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surfaces, based on the changes of optical properties, is defined. In this work, tests for assessing the thermal stability of absorber surfaces with high-temperature ageing will be studied to analyse the degradation of the selective paint structure when subjected to temperature exposure. High temperature accelerates many processes, generally leading to an increased rate of degradation of materials. For selective absorber coating composed of small metal particles, high temperature leads to oxidation of the metal decreasing the absorptance of the coating. An absorber surface, installed in a flat plate solar collector, is exposed to extreme temperatures that may vary between -20°C to over 200°C, according to ISO 22975-3:2014 [16]. The referred test is processed in an ageing chamber. From the point of view of ageing by temperature, it is only on sunny days, when the collector is under stagnation, that the temperature load results in degradation.

11 MATERIALS AND METHODS

11.1 COATINGS

Two types of commercial selective paint coatings were used in this study, both deposited in an aluminium substrate. PC2 with a silicone binder and PC3 with a polyurethane binder. PC2 is thickness sensitive spectrally selective (TSSS) paint coatings (commercial names: SUNCOLOR TS S Black and SOLKOTE HI/SORB-II ™) and PC3 is a thickness insensitive spectrally selective (TISS) type paint coating (commercial name: SUNCOLOR PUR Black) containing metallic pigments. The paints were applied on aluminium substrates according to the products technical instructions. [4].

11.2 ACCELERATED AGEING TEST – TEMPERATURE

The absorbers were tested at 320°C for a total time of 600h in an oven Thermo Scientific Heratherm OMH 100. Optical properties were determined after 18, 36, 75, 150, 300 and 600h. FTIR analysis was performed after 300 and 600h and TGA and SEM/EDS after 600h.

11.3 OPTICAL PROPERTIES

The absorber surface samples were initially optically characterized by measurement of solar absorptance (α_s) and thermal emittance (ε_t).

11.3.1 Absorptance

Absorptance (α_s) is a fraction of solar radiation energy absorbed by an absorber surface [19], is defined by the Eq 4. [2].

$$\alpha_s = \int_0^\infty \frac{[1-p(\lambda)]S_\lambda}{S_\lambda} d\lambda \qquad \text{(Eq. 2)}$$

where S_λ is the spectral solar irradiance according to ASTM G173 − 03(2012), $p(\lambda)$ is spectral hemispherical reflectance of absorber coating between 300 to 2500nm [2].

Procedure

The solar absorptance (α_s) was determined based on the solar absorption hemispherical solar spectral irradiance (incident on a 37° tilted plane, equator-facing) and the reflectance measurements were done on Perkin Elmer Lambda 950 UV/VIS/NIR with a 150 mm integrating sphere. [2], [4]

11.3.2 Thermal emittance

Thermal emittance (ε_t) is the ratio between the energy per unit area radiated by a surface at a given temperature and the corresponding energy radiated by a perfect black body at the same temperature [19]. This ratio is defined by Eq. 5 [2].

$$\varepsilon_t = \int_0^\infty \frac{[1-p(\lambda)]P_\lambda(T)}{P_\lambda(T)} d\lambda \qquad \text{(Eq. 3)}$$

where $p(\lambda)$ is the spectral hemispherical reflectance of absorber coating between 2.5 and 40 μm and, $P_\lambda(T)$ is the Planck function for a black-body at a temperature T equal to 373 K [15, 16].

Procedure

Thermal emittance values were usually analysed in the infrared region between 2.5–20 μm [10]. The thermal emittance was determined with an IR/NIR of Perkin Elmer Frontier, using an integrating sphere, allowing the reflectance spectra shown to be drawn [2, 4].

11.3.3 Performance Criterion

Evaluation of absorber coatings is based on a performance criterion directly dependent on the optical properties of the collector and which is defined according to Eq. 6 [2, 21].

$$Pc = -\Delta\alpha_s + 0.5\Delta\varepsilon_t \qquad (Eq.\ 4)$$

where $\Delta\alpha_s$ is the change of solar absorptance during an ageing test and $\Delta\varepsilon_t$ the change in thermal emittance. In order to an absorber coating to be qualified, the value of Pc should be equal or lower than 0.05, according to ISO 22975-3:2014 [19].

11.4 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared spectroscopy relies on the fact that molecules are in a constant state of motion. Molecules are constantly undergoing both bending (change of bond angle) and stretching (change of bond length) vibrations. An infrared spectrum is obtained by focusing a beam of IR radiation through a sample and then observing the frequencies at which the sample absorbs in each wavenumber. The spectra can be transmission and absorption. In this work was done transmission for the binder of the coatings and ATR for the coatings because they have black pigments and for that reason FTIR-ATR was the most adequate technique.

11.4.1 Transmission

Fourier-Transform infrared spectrometers are based on the interference of radiation between two beams to produce an interferogram. This is achieved with an infrared (IR) radiation source, an interferometer, the sample and a detector [22, 23]. The most common interferometer used is the Michelson interferometer, as shown in the following figure.
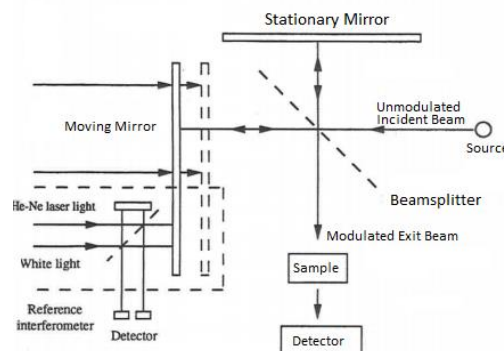

Figure 4 - Schematic representation of a Michelson interferometer (adapted from [23])

With this instrument, the infrared radiation stemming from the source passes to the sample (some radiation is absorbed, some is transmitted) through the interferometer before reaching the detector. The resulting signal at the detector is a spectrum representing a molecular 'fingerprint' of the sample [23, 24]

In the interferometer, composed of a beam splitter and two mirrors (one stationary and one moving), the radiation beam is divided, causing 50% of it to go to the fixed mirror and 50% to the moving mirror. These two beams are then reflected from the two mirrors to the beam splitter and recombined. If it is verified a zero-path difference (ZPD) the beams interact in phase and reinforce each other; if this does not happen, the beams interact destructively [22, 23, 25]. Interferometry produces a complex waveform that adds the contribution of all wavelengths emitted by the radiation source, producing the interferogram that is mathematically treated with the Fourier transform equation (Eq. 7) to give rise to an infrared spectrum.

$$I(v) = \int_{-\infty}^{+\infty} I(t)e^{(i2\pi vt)}dt \qquad \text{(Eq. 5)}$$

where I(v) is frequency intensity, I(t) is the interferogram amplitude and $i = \sqrt{-1}$ [22].

For measurements in the middle infrared region there are two commonly used detectors, a pyroelectric device incorporating deuterium triglycine sulphate (DTGS) and a semiconductor composed with a mercury-cadmium-telluride alloy (MCT) [22, 23].

11.4.1.1.1 Procedure

To identify the binders of the selective paints, the binders which were previously separated from the volatile vehicle and from the pigments, were analysed by FTIR spectroscopy (transmission). Spectra were obtained on a Perkin Elmer Frontier spectrometer in the range 4000-400cm^{-1}, with 4cm^{-1} resolution and 32 accumulations. Samples were analysed over a sodium chloride (NaCl) window after evaporation of the solvent.

11.4.2 Attenuated Total Reflectance (ATR)

One way of obtaining a spectrum of a solid, a paste or a viscous liquid is by attenuated total reflectance (ATR). In ATR experiments, significant energy losses occur [25]. This type of spectroscopy uses the phenomenon of total internal reflection shown in the figure 5.
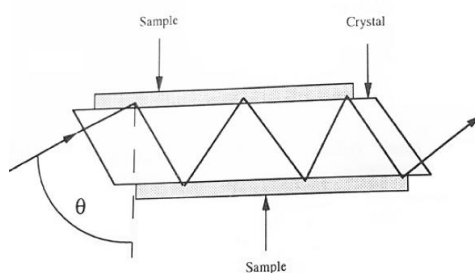
Figure 5 - Schematic representation of total internal reflection [23].

A radiation beam is focused into the crystal, which must be made of materials that have low solubility in water and very high refractive index (such as zinc selenide, germanium or thallium/iodide). Total internal reflectance occurs when the incident angle is higher than a critical angle (function of the refractive indices of the two surfaces). As shown in $n_1 = n_2 \times \sin(\alpha_c)$, where n$_1$ is the refractive index of the crystal, n$_2$ is the refractive index of the sample and α_c is the critical angle.

This beam penetrates one fraction of wavelength beyond the reflector surface. It loses energy in a wavelength where the material absorbs – this happens in a material that selectively absorbs radiation in contact with a reflective surface[23, 25].

11.4.2.1.1 Procedure

Coatings were analysed by FTIR-ATR before and after 300 and 600h ate 320. Spectra were recorded on a Thermo Nicolet 6700 Spectrometer with sampling accessory (Smart iTR) having a single bounce diamond crystal. The spectra were acquired with a 45° incident angle in the range of 4000–525 cm^{-1}, with a 4 cm^{-1} resolution and 32 accumulations. Spectra were taken in several different zones of the sample. For the analysis, for each sample only one of the spectra was considered, since they were very similar.

11.5 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis (TGA) determines the quantity and frequency of the weight variation of the samples as a function of temperature and time in a controlled atmosphere [26], [27]. This analysis can be used to determine the temperature and rate of decomposition of polymers, and to measure at the same time the amounts of volatile matter, additives and/or fillers they contain [28]. The change in mass as a function of temperature and the extent of this change are indicators of the thermal stability (the strength of the material at a given temperature [26]) of the material and the assessment of thermal stability is one of the most important applications of TG to the study of polymer [28, 29]. TGA is especially important in applications that use polymeric materials such as coating material for electrical and electronic components, paints, pharmaceuticals, petroleum, adhesives, among others [26].

Thermogravimetric analysis can be executed in an inert atmosphere (nitrogen, for instance) or with an oxidative atmosphere. TGA in inert atmosphere, although not a sufficient test of thermal stability, allows for empirically comparing experimental polymers of broadly divergent chemical nature and decomposition mechanism [30]. During the process can occur weight losses or gains. The weight loss can occur because of decomposition (the breaking apart of chemical bonds), evaporation (the loss of volatiles with elevated temperature), reduction (interaction of the sample to a reducing atmosphere) and desorption. The case of weight gain, can occur when the sample suffers oxidation (interaction of the sample with an oxidizing atmosphere) or absorption [27].

This process is easy to set up and when the individual decomposition steps occur at well separated temperatures, quantitative information for each step can be obtained. However, it can have complex thermal scans with broad weight losses and overlapping weight losses with multiple peaks/shoulders, may be obtained [27].

11.5.1.1.1 Procedure

In this work the stability of the coatings PC2 and PC3 in air was investigated by TGA performed in oxidative atmosphere (air). In order to evaluate the degradation caused by the accelerated ageing test samples of the coatings non subjected to thermal ageing and after 600 h at 320°C were analysed in inert atmosphere (N$_2$). The two procedures were executed from room temperature to 850°C Thermogravimetric analyses were performed on a TG-DTA/DSC

Setsys-1750 (Setaram) equipment, with a sensitivity of 1µg and temperature accuracy of 0.001. The sample (±10mg) was placed in an alumina crucible.

11.6 SCANNING ELECTRON MICROSCOPY (SEM) WITH ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

A scanning electron microscope uses a finely focused beam of electrons to reveal the detailed surface characteristics of a specimen and provide information relating to its three-dimensional structure. The equipment can have a resolution of 1 nm.

When a fine beam of electrons is focused on the surface of a specimen, different interactions occur, including the emission of secondary and backscattered primary electrons. If these are collected and amplified, they can be used to create an image corresponding to the surface topography of the specimen. The electron beam is scanned across the specimen repeatedly in a raster pattern, which is synchronized with the scan of a cathode ray tube such that the image is presented in a digitized form built up on a TV monitor. As with transmission electron microscopes, conventional instruments must be operated under high vacuum in order that the electron beam can travel to the specimen surface [31].

In this work, secondary electron (SE) and backscattered-eletron (BSE) detectors were used. The microstructures and morphology were analysed from initial and aged coating samples.

11.6.1.1.1 Procedure

The morphology of the absorber surfaces of PC2 and PC3 at 0h and 600h at 320°C was examined using a Philips Scanning Electron Microscope, Model XL30 FEG-SEM with Energy Dispersive X-ray Spectroscopy (EDS) associated. The samples were previously goldcoated for better conduction, in an Emitech K575X turbo sputter coater, for 10 s.

12 RESULTS AND DISCUSSION

The accelerated ageing tests caused degradation of the absorber coatings. The ageing mechanisms have been analysed through changes in optical properties composition (FTIR and TGA), and microstructure (SEM/EDS), before and after exposure at 320°C.

12.1 OPTICAL PROPERTIES

The following graphs present the average values of solar absorptance and thermal emittance for the initial PC2 and PC3 samples, after having been subjected to the accelerated ageing test for 18, 36, 75, 150, 300 and 600h at 320°C. The calculations were performed using equations 2 and 3.
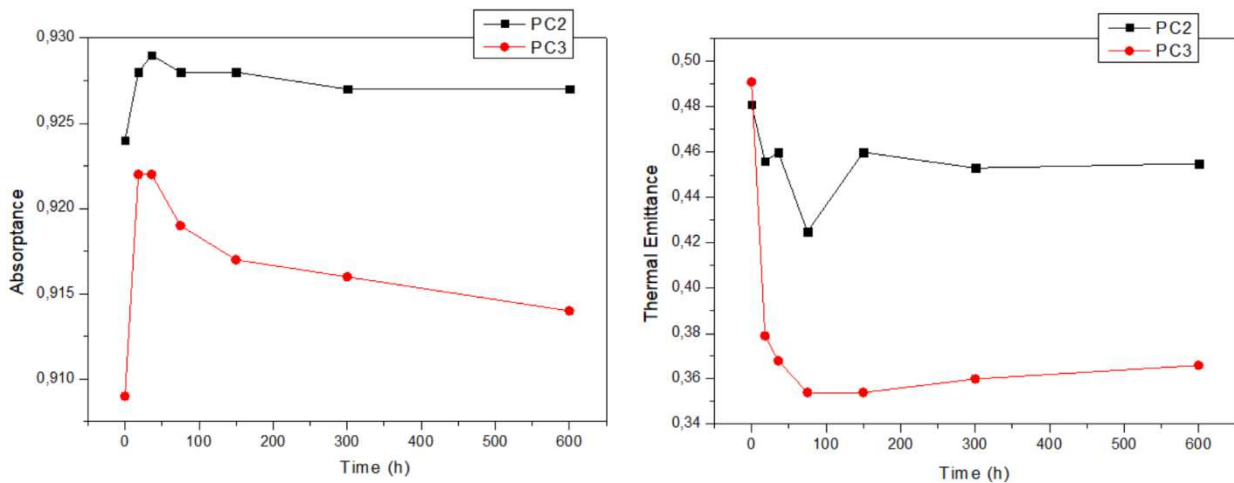
Figure 6 – Absorptance and Thermal Emittance of PC2 and PC3 over time

The absorptance values over time show similar behaviour in both cases. During the first 18h (PC3) and 36h (PC2) of testing, an increase in the absorptance, more notable in the case of PC3, is observed, followed by a progressive decrease of the absorptance until 600h of testing. Despite this decrease, the final value, after 600h, is higher than the initial absorptance, in both cases. This is a positive result, because for a coating to be spectrally selective it is mandatory to have high absorptance, *i.e.* absorb near 100% of the short wavelength radiation.

Thermal emittance of PC3 shows an initial steep decrease, stabilizing at 75h. The value then increases steadily, until 600h. Regarding PC2, a similar yet more irregular behaviour takes place. The thermal emittance also decreases steeply until 75h (note that the measurement at 36h indicates a slight increase, but it can be considered an experimental error). After 75h, the general tendency is of increasing the value, starting at around 0.42 and ending at around 0.45. It is important to comment on the experimental measurement at 150h. The value was predicted to be only slightly smaller than at 300h, seeing that the absorptances of both paints evolved in a similar way. However, this does not happen, with the value at 150h being much higher than at 75h and even slightly higher than at 300h. This can be considered an experimental error; indeed, the absorptance of PC2 at 150h also seems to be higher than the expected value, given the observed trend. Globally, both paints reduce their thermal emittance values when comparing the initial and final results.
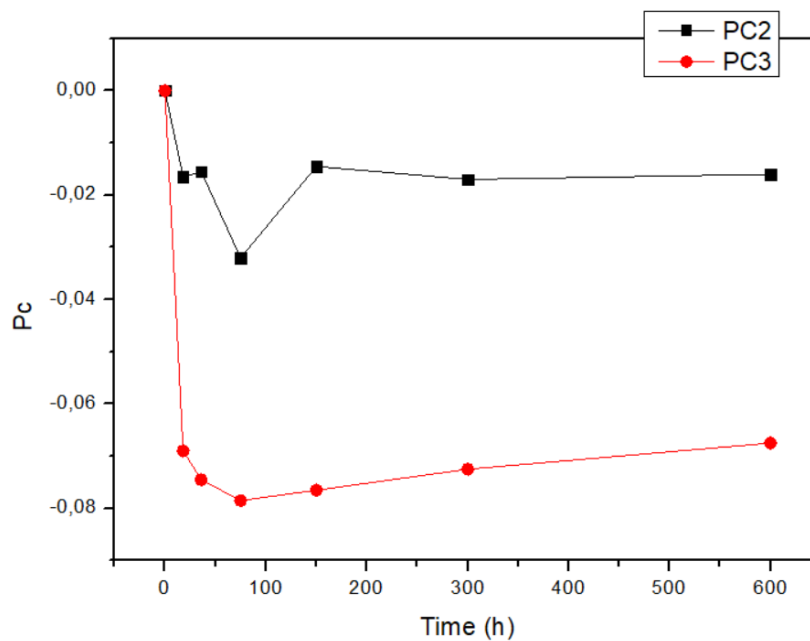

Figure 7 - Performance criterion (equation 4) of PC2 and PC3 over time

The values of PC over time (Figure 7), vary in the same way as the thermal emittance for both coatings. Over time, and for both coatings, the PC is always less than 0.05 so these coatings obey the qualification requisite of PC to withstand a maximum temperature of 320 ºC.

12.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

12.2.1 Polysiloxane based coating - PC2

12.2.1.1 Binder – FTIR transmission

The spectrum of the PC2 binder (figure 8) shows characteristic bands of polysiloxanes. Besides the two maxima at 1087 cm^{-1} and 1030 cm^{-1} assigned to ν(Si-O) and common to polymeric siloxanes [32, 33], the spectrum contains information about the functional groups attached to Si atoms.
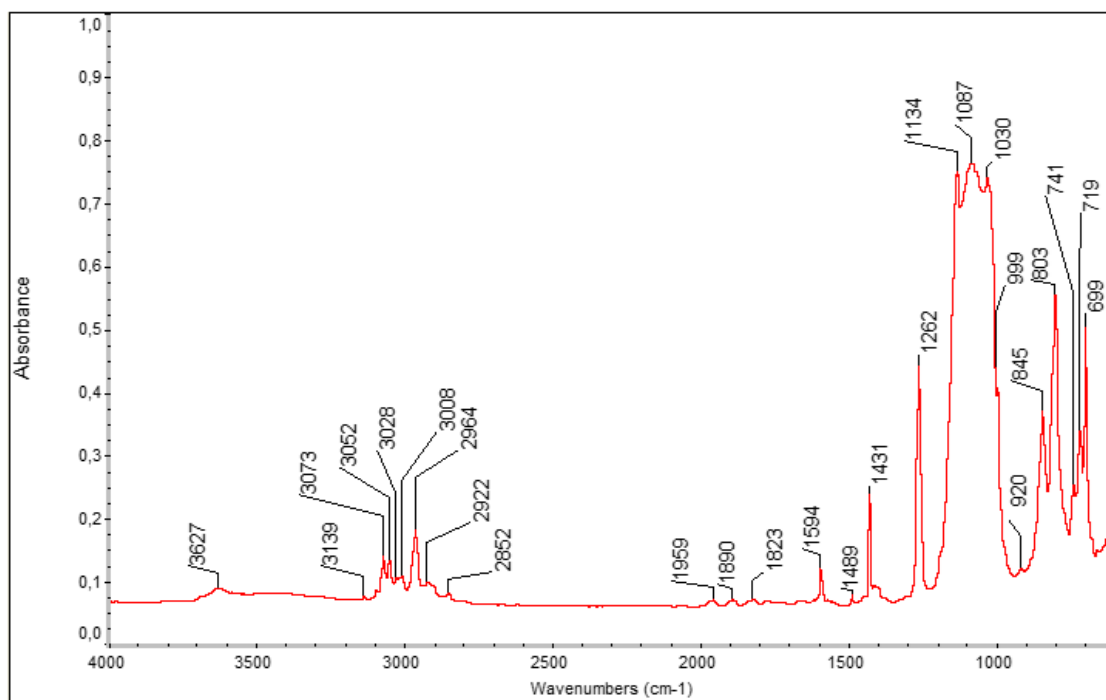

Figure 8 – Transmission FTIR spectrum of PC2 binder in the region 4000-600 cm^{-1}.

As shown in the graph of figure 8, the peaks at 3073 - 3008cm^{-1} and 2964-2852cm^{-1} are associated with the ν(C$_{sp2}$H) and ν(C$_{sp3}$H). C$_6$H$_6$ is identified in the range 1959-1823cm^{-1} by three weak peaks [34], [35].

In polysiloxanes, the presence of Si(CH$_3$)$_2$ is recognized by a strong, sharp band at about 1260cm^{-1} (in this case, 1262cm^{-1}), associated with δ(CH$_3$) in Si(CH$_3$)$_2$ together with one or more strong bands in the range 865-750cm^{-1} (in this case, at 803 and 845cm^{-1}). The graph from figure 8 shows the described conditions, confirming the presence of Si(CH$_3$)$_2$ groups.

The presence of a phenyl group attached to an Si atom is recognised by the presence of the bands at 1594cm^{-1} and 1431cm^{-1}, which are associated with ν(ring) of a phenyl group. The presence of this aromatic structure is also confirmed by the bands at 3073cm^{-1} and 3052cm^{-1}, which are associated with ν(CH) in aromatic rings. The presence of the bands already mentioned as well as the presence of the bands at 1134cm^{-1}, 845cm^{-1}, 741cm^{-1} and 699cm^{-1}, indicate that the binder is probably a poly(dimethylsiloxy-co-methylphenylsiloxane) [32], [33], [36].

12.2.1.2   PC2 in the beginning, PC2 320°C 300h and PC2 320°C 600h

Figure 9 shows the comparison between the spectra of binder and initial PC2.
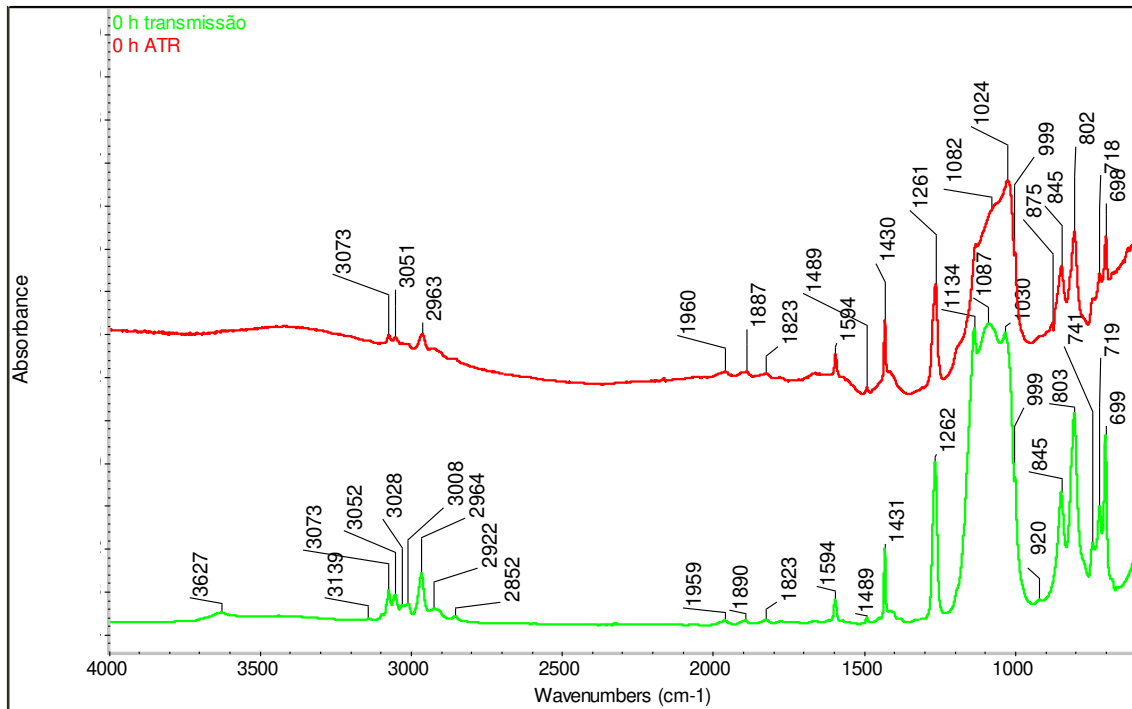
Figure 9 – FTIR-ATR spectra of PC2 binder (green) and PC2 coating (red) at 0h in the region 4000-400cm⁻¹

In the spectrum of the initial PC2 (Figure 9 – red) it was possible to identify the bands corresponding to those of the binder (Figure 9 – green). The only significant change was in the binder's bands at 1134cm⁻¹, 1087cm⁻¹, and 1030cm⁻¹, corresponding to the highest-intensity bands. These bands, in the binder, have similar intensities, even though the band at 1087cm⁻¹ corresponds to actual maximum. In contrast, in the PC2 coating, these bands' intensities increase with the decrease of wavenumber. Specifically, the baseline absorbance at 1128cm⁻¹ is smaller than at 1082cm⁻¹, which is also smaller than at 1027cm⁻¹. This shows the difference between the bands of the binder and coating.

The spectra of the initial PC2 sample and after ageing at 320°C (300h and 600h) were obtained, using FTIR-ATR, shown in figure 10.
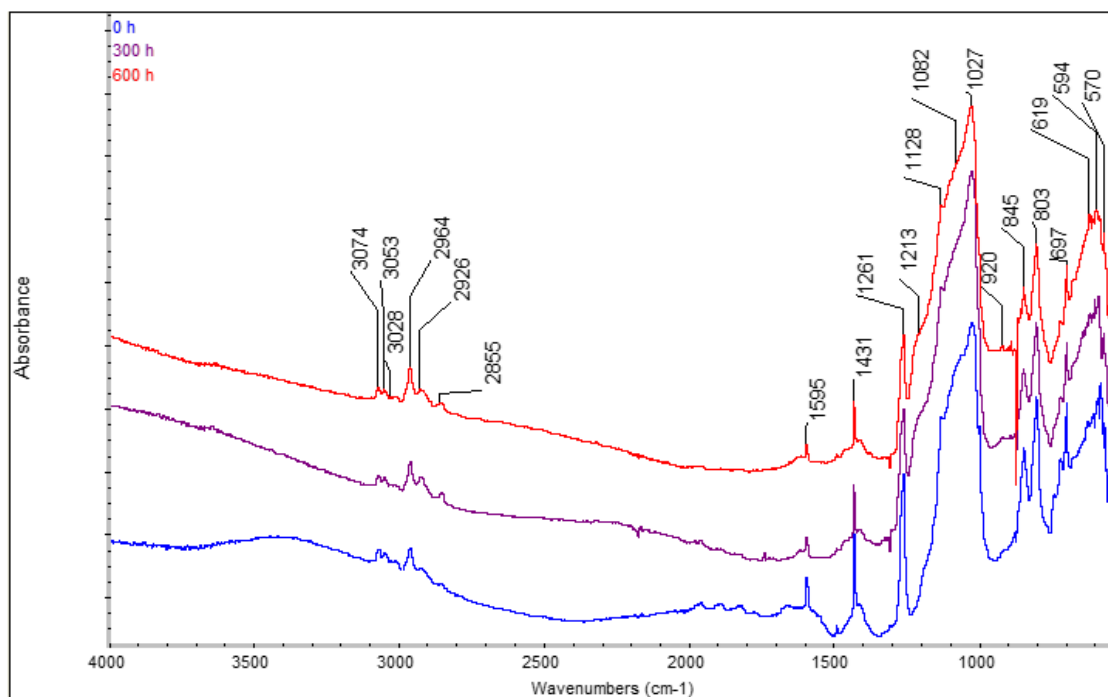
Figure 10 – FTIR-ATR spectra of PC2 coating after 0h, 300h and 600h at 320°C

There is no considerable variation when the samples are subjected to thermal stability tests. The coatings's spectra shows a decrease in the intensity of the bands at 1595cm^{-1} associated with v(C=C), 1431cm^{-1} associated with v(ring), and 1261cm^{-1} associated with Si(CH$_3$)$_2$, related to the bands in the v(CH) region. Also, the appearing of a shoulder in the left of the band at 1128cm^{-1} associated with Si-0, was observed.

This could mean that there was no significant alteration of the coating's structure during the application of temperature, even for long periods of time. While there were a few specific alterations, as seen by the differences between the spectra at 0h, 300h, and 600h, these are not significant, and do not greatly affect the coating as a whole.

12.2.2 Polyurethane based coating - PC3

12.2.2.1 Binder – FTIR transmission

To analyse its structure, an analysis of the FTIR spectrum of PC3 binder was carried out.

Figure 11 – Transmission FTIR spectrum of PC3 binder in the region 4000-600 cm^{-1}

In the case of PC3 sample, the expected binder was polyurethane. Even though the detailed molecular structure of the polyurethane resin binder was not provided in sufficient detail from the manufacturer and despite its expected complex structure, it was possible to link certain vibrational bands between the po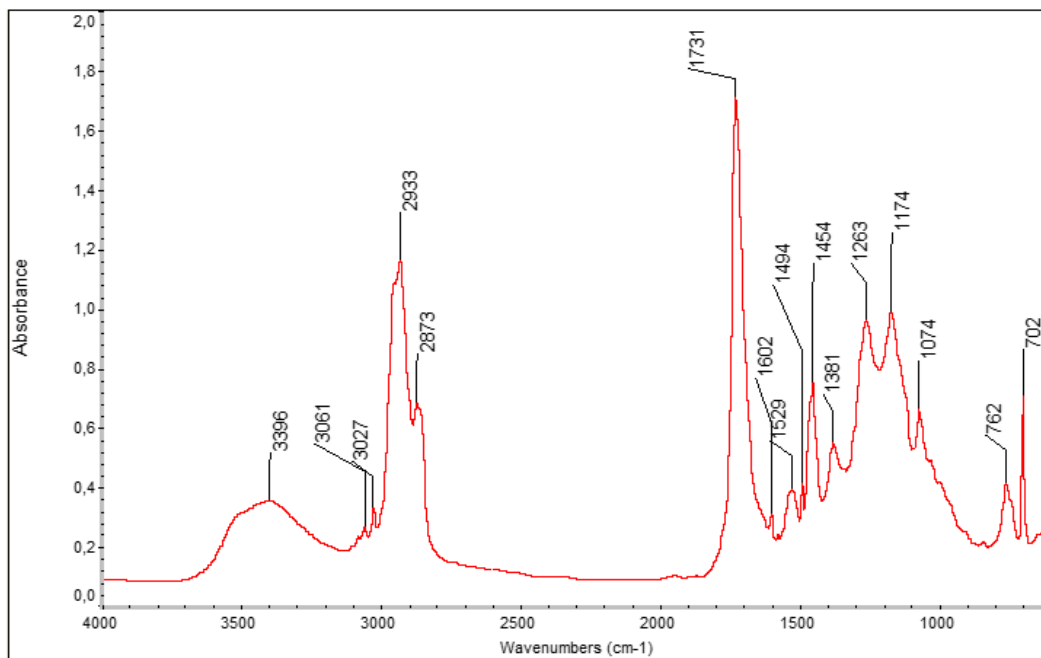lyurethane and the used binder [37, 38]. Specifically, polyurethane is recognised mainly by the bands at 1529cm^{-1}, and 762cm^{-1}.

Another possible polymer that fits the spectrum of the used binder is poly(styrene acrylate ester) [32, 33].The styrene group is recognised by the presence of the bands at 1494cm^{-1}, 762cm^{-1}, and 702cm^{-1}, and by the polyacrylic esters is recognized by the characteristic bands at 1731cm^{-1}, 1263cm^{-1}, and 1174cm^{-1} [32, 33].

In the literature, it is possible to identify poly styrene acrylate ester as an element used in the preparation of polyurethane-based coatings used for corrosive protection of surfaces, which may be the explanation for the identification of characteristic bands of this polymer in the polyurethane spectrum [42].

The bands belonging the high wavenumber region correspond to the backbone (-CH$_2$-chain mode bands at 2933 and 2873 cm^{-1}) of the polymer, while the bands in the lower wavenumber region (1800-850 cm^{-1}) are assigned to less stable bonds, -C=O (1731 cm^{-1}) and ν C-N + δ N-H (1529 cm^{-1}) of the urethane linkages, ν C-O-C in ester (1174-1074 cm^{-1}) and δ oop in COO urethane (762 cm^{-1}) [32, 33, 37, 38].

12.2.2.2 PC3 in the beginning, PC3 320°C 300h and PC3 320°C 600h

Figure 12 shows the comparison between the spectra of binder and initial PC3.
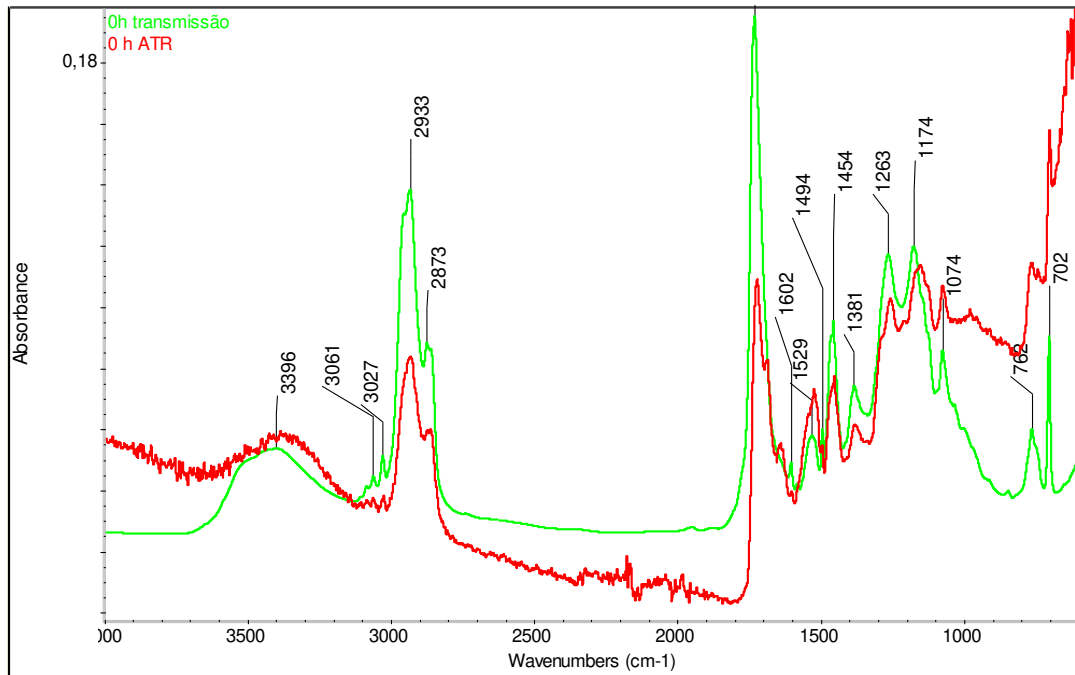
Figure 12 - FTIR-ATR spectra of PC3 binder (green) and PC3 coating (red) at 0h in the region 4000-400cm-1

Figure 12 shows that the bands of the spectrum of the PC3 binder match the bands of the PC3 coating. No discernible peaks were unmatched between the spectra.

The spectra of the initial PC3 sample and after ageing at 320°C (300h and 600h) were obtained, using FTIR-ATR, shown in figure 13.
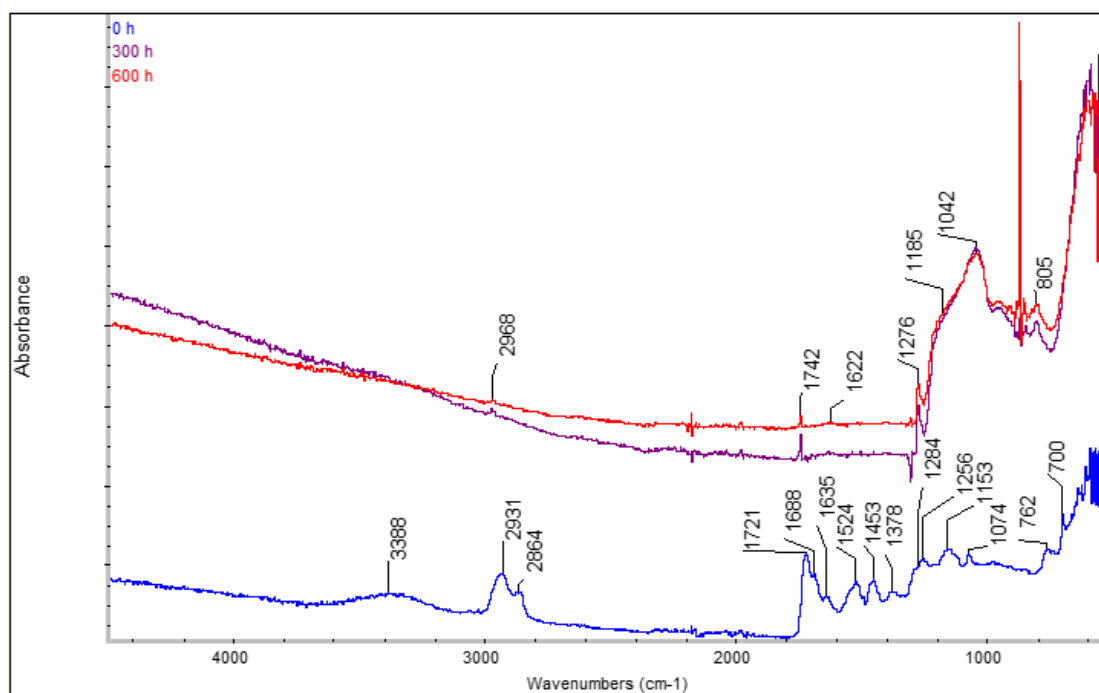
Figure 13 – FTIR-ATR spectra of PC3 coating after 0h, 300h and 600h at 320°C

Figure 13 shows the FTIR-ATR spectra of PC3 in the beginning, after 300h and after 600h. When the coating was subjected to temperature there was the degradation of the polymer used as a binder. This degradation is evident by the loss of binder, represented in the previous graph, thus showing that over the time of exposure the polymer will degrade, and the pigments will be more exposed to environmental factors.

Comparing the initial spectra with the spectra of the samples subjected to temperature tests at 320°C it is possible to identify the loss of polymer by *e.g.*, ν C=O in ester at 1721 cm^{-1}, ν C=O associated in urethane at 1688 cm^{-1}, ν C-N + δ N-H (amide II) at 1524 cm^{-1} and ν C-O-C in ester at 1256 and 1153 cm^{-1}[38].

12.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

12.3.1 Polysiloxane based coating - PC2

12.3.1.1 Oxidative atmosphere

The thermogram of PC2 (Figure 14) under oxidative atmosphere shows two zones of mass loss, one beginning at around 50°C and ending at around 425°C, and the other starting thereafter and ending at around 575°C. During the first zone the sample loses 6.71% of mass, while during the second zone it loses around 7.21%. The accumulated mass loss is 13,92%. After this temperature no significant mass loss occurs. This thermogram presents the thermal stability of PC2 up to 50°C.

Figure 14 - Thermogravimetric curve of PC2 initial samples in oxidative atmosphere

12.3.1.2 Inert atmosphere

Figure 15 - Thermogravimetric curve in inert atmosphere of PC2 initial samples (left) and after 600h at 320ºC (right)

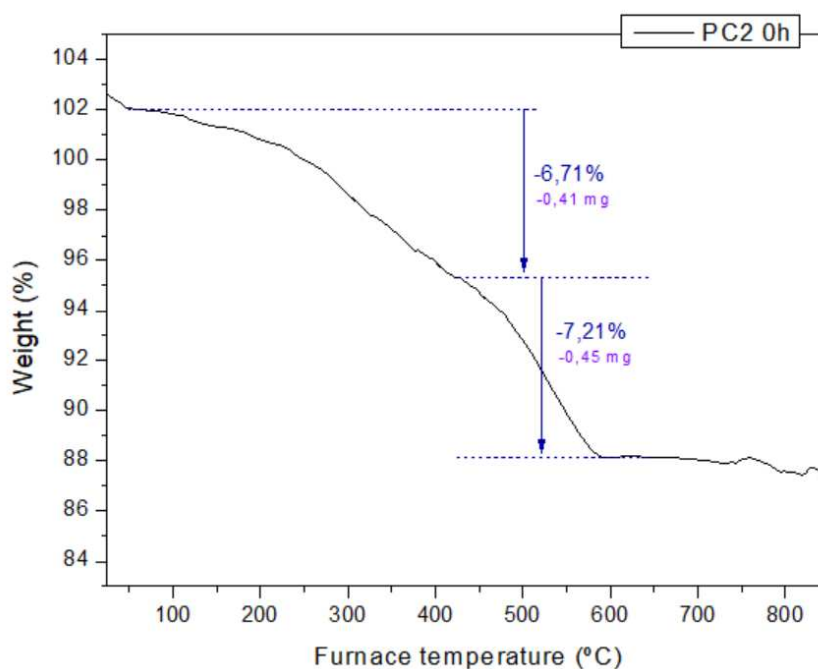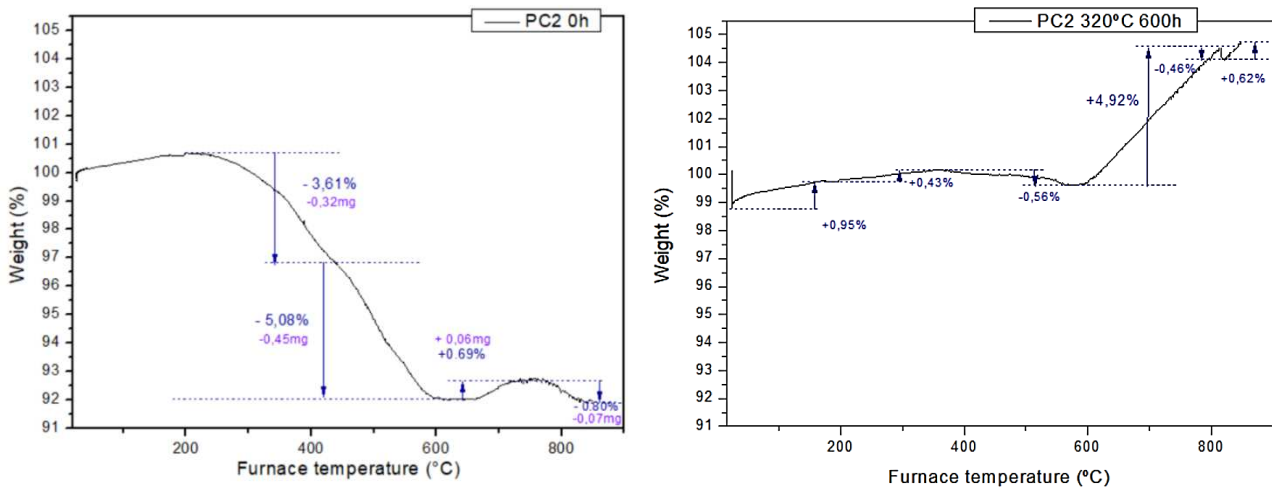The thermogram of the initial PC2 under inert atmosphere (Figure 15 – left) shows two zones of mass loss. The first zone starts at around 200ºC and ends at around 425ºC (weight loss of 3.61%), and the second starting thereafter and ending at around 600ºC (weight loss of 5.08%). The combined mass loss is of 8.69%. The shown loss of mass between 200°C and 600°C can be justified by the loss of polymer – polysiloxane. In the literature [39] it is shown that tests performed on polysiloxane denote a polymer loss of about 80- 90%. These losses are noticeable in the same range of temperatures as in the PC2 sample.

The thermogram of the PC2 sample subjected to 320°C for 600h (Figure 15 – right) shows a mass loss of 0.56% between a temperature around 335°C and 570°C, which is the highest range of mass loss observed in the initial PC2, and an increase of mass from around 600°C until 850°C. Considering that FTIR-ATR spectra did not indicate significative changes in the binder after 600h at 320°C, a possible explanation for the mass loss of only 0.56% observed in this thermogram may be that the fraction of sample analysed had a higher pigment fraction than that of the initial PC2 sample. In this thermogram no mass loss at lower temperatures was observed showing that components of the coatings, eventually additives and/or degradation of the polymer has occurred in some extent during the accelerated ageing treatment as was expected from data in Figure 10.

Based on the literature, when the TSSS paint is applied, the paint layer is very thin and curing time is usually processed 30—40s at 300°C. A small percentage of mass loss can be a consequence of the incomplete curing process of the silicon resin binder due to the short curing period [40]. However, and considering the analysis of the graph in oxidative atmosphere, it is also possible to consider that there is loss of polymer during the test up to 600°C.

12.3.2 Polyurethane based coating - PC3

12.3.2.1 Oxidative atmosphere

The TG measurements (Figure 16) showed that the temperature stability of the resin binder was limited to a temperature below 240°C. PC3 exhibited a single step decomposition process, starting at 240°C and ending at 400°C, where the mass loss was 27.88%.
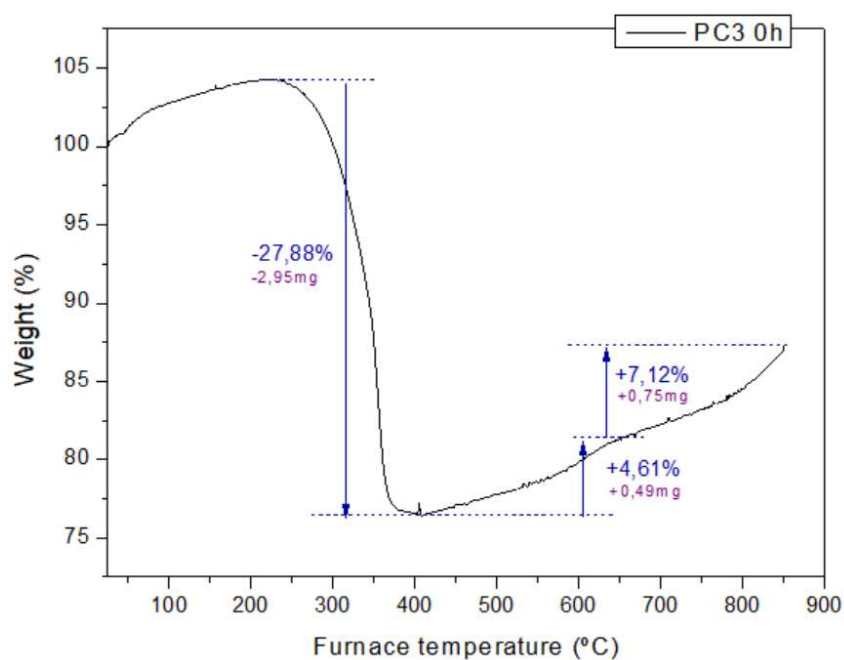
Figure 16 - Thermogravimetric curve of PC3 initial samples in oxidative atmosphere

This loss of mass is associated with the degradation of the polymeric binder, thus supporting the results obtained in FTIR-ATR. This steep reduction of the polymeric binder exposes the pigments to the atmosphere. After the degradation, a two-phase mass gain occurs, from 400°C to 850°C, corresponding to a weight increase of 11.73%. This thermogram present the thermal stability of PC3 up to 240°C.

12.3.2.2 Inert atmosphere

The TG measurements showed that the temperature stability of the resin binder was limited to a temperature below 230°C. The observed weight reduction took place in two stages, one starting at 230°C and ending at around 325°C (with a weight loss of 13.15%), and the second starting thereafter and ending at around 500°C (with a weight loss of 16.47%).
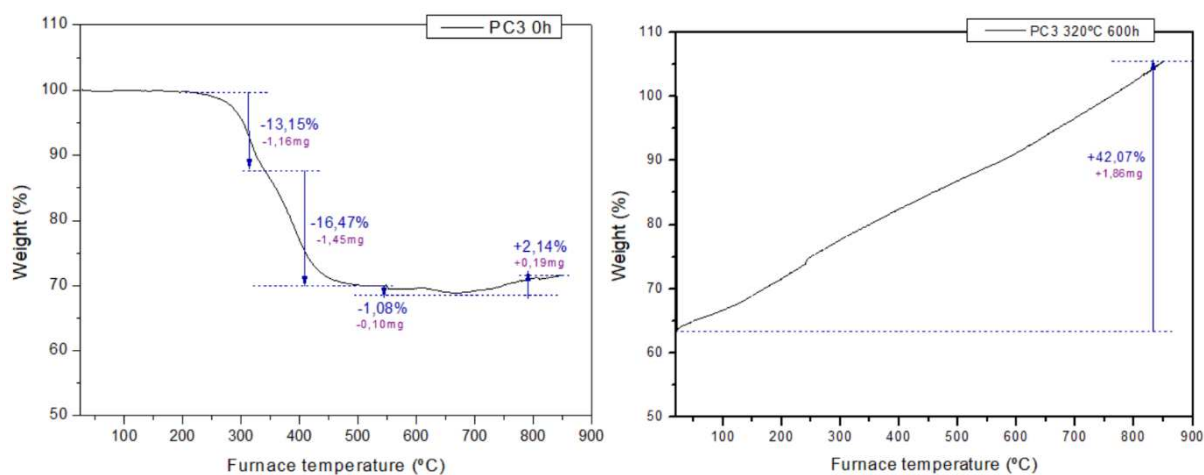
Figure 17 - Thermogravimetric curve in inert atmosphere of PC3 initial samples (left) and after 600h at 320°C (right)

After the sample has been subjected to accelerated ageing for 600h at 320°C, its thermogravimetric graph changes completely when compared with the sample that was not been subjected to temperature testing. No mass decrease was observed, supporting the results of FTIR-ATR spectra that extensive degradation of the binder occurred, and in accordance with the result of the TG analysis in air. Instead, an approximately linear increase of the mass in relation to the increase in temperature took place.

During the ageing, a degradation of the polymeric binder present in PC3 was noticed. As there is degradation of the polymer, the pigments are immediately exposed to the atmosphere; for this reason, the increase in mass can be related to the oxidation or absorption of molecules existing in the atmosphere by the pigments [27].

When preparing the PC3 320°C 600h samples for the test, the cohesion between the pigment particles was partially lost, at least on the upper pigment layer of the coatings, leading to an easier extraction of the coating from the substrate. This demonstrates the loss of binder that took place during the ageing tests – smaller quantities of binder results in a lower cohesion between the pigments.

12.4 SCANNING ELECTRON MICROSCOPY (SEM)

12.4.1   Polysiloxane based coating - PC2

SEM micrographs of the PC2 coating not subjected to thermal treatment (Figure 18) revealed that the paint coatings are characterized by a smooth surface without any of the pigment particles protruding out from the surface of the coating. The image bellow presents the surface of PC2 samples in SE.
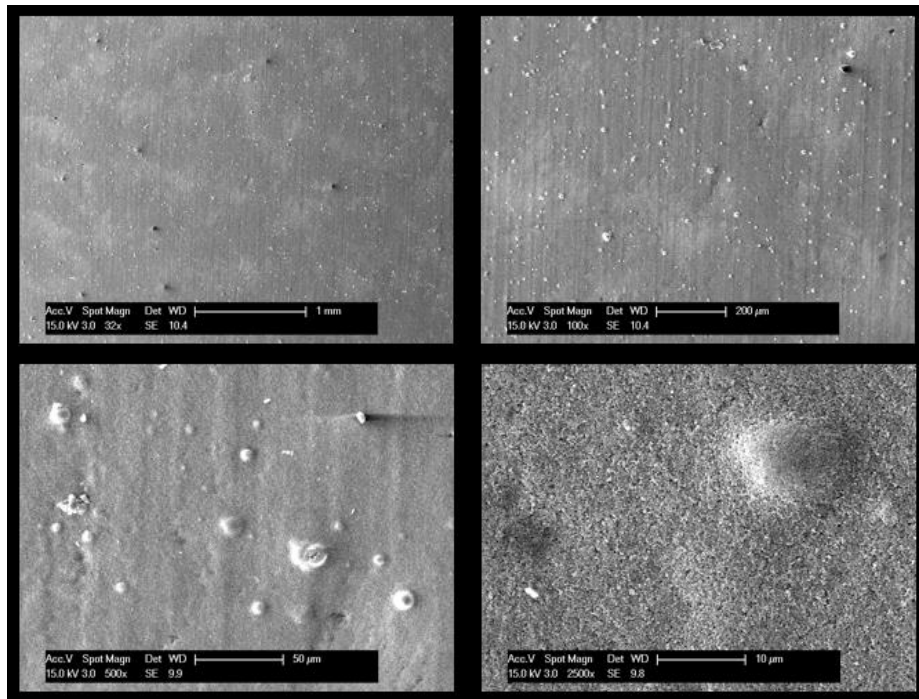
Figure 18 – Top view SEM micrographs of PC2 initial sample

These imagens show small holes which are randomly distributed and may have been caused by an overly fast evaporation of the solvent during curing and/or by too high curing temperatures of the coatings. These holes could be avoided by either decreasing the surface tension of the paint, or by decreasing the curing temperature and by substituting the existing solvent with another having a higher boiling point [41].

The effect of thermal ageing of the PC2 (silicone) coating was studied by analysing the structure in SEM.
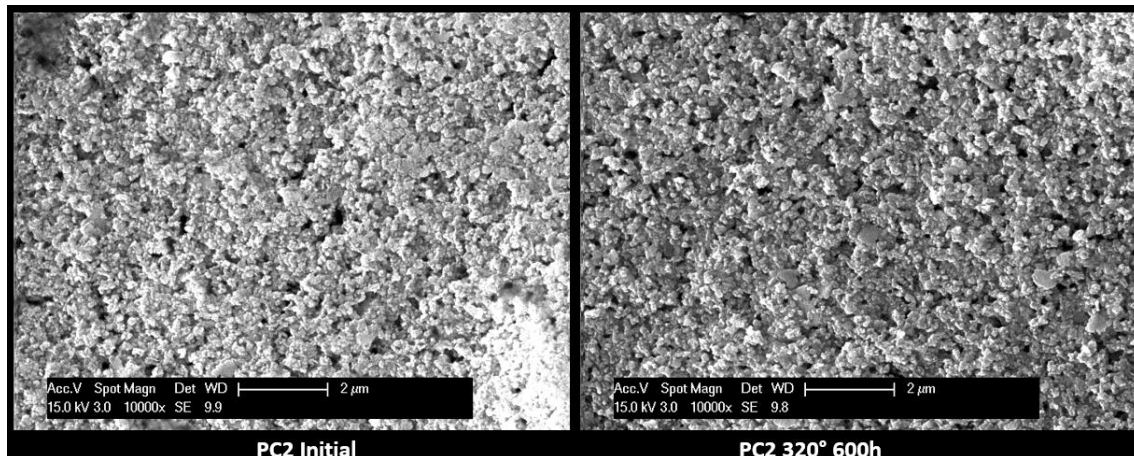
Figure 19 - SEM micrographs of initial PC2 and PC2 320°C 600h

The structure of the initial PC2 compared to the structure of the PC2 after the ageing test (Figure 19) has similar characteristics. In both cases it is possible to see the pigments (containing aluminium, Al, copper, Cu, manganese, Mn, and iron, Fe) – the pigments have a spherical shape. The main difference in the structure after ageing is that the spaces between pigments are less filled, thus suggesting that there was a slight loss of polymer during temperature tests.
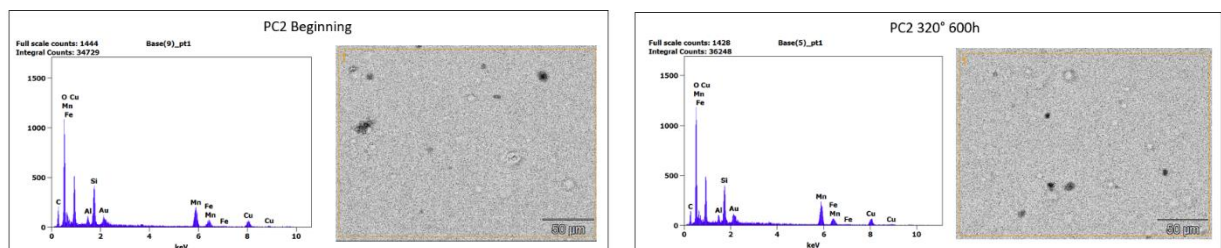
Figure 20 - EDS spectrum of PC2 initial sample and PC2 320°C 600h.

The EDS spectra of PC2 and PC2 320°C 600h (Figure 20) showed that the constituent elements of the sample did not change after the ageing process, and that their proportions remained approximately the same. This result is in agreement with the results of FTIR-ATR, thus showing that in PC2 even after temperature tests there was no significant degradation in the structure of this selective paint.

12.4.2   Polyurethane based coating - PC3

The effect of thermal ageing of the PC3 (polyurethane) coating was studied by analysing the structure in SEM.
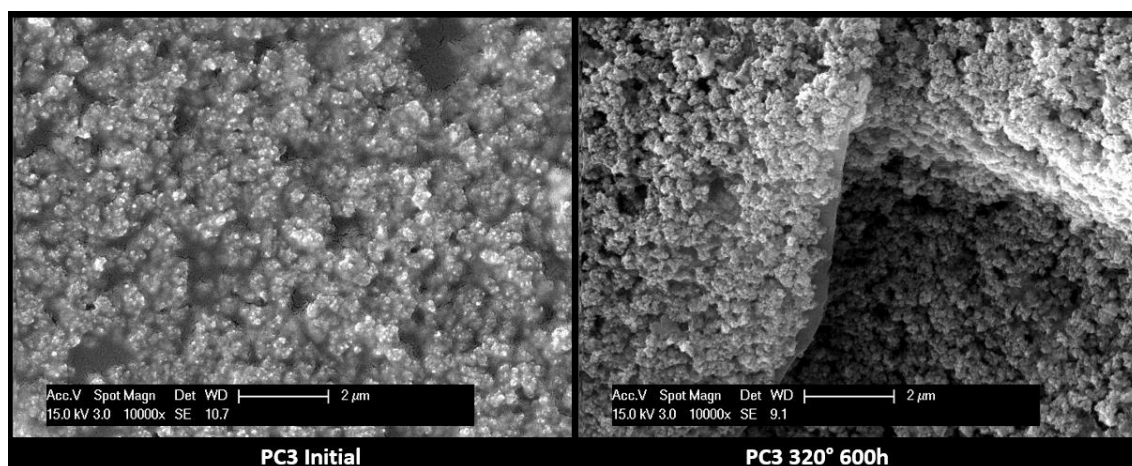
Figure 21 - SEM micrographs of initial PC3 and PC3 320°C 600h

SEM analysis of the initial sample showed metallic flakes (pigments) and polymeric binder (Figure 22). Aged PC3 sample exhibits an additional fine structure, attributed to the pigment particles on the flakes' surface. The surface of the sample is mostly constituted by pigment since most of the superficial binder was degraded during the ageing process. As shown in figure 22 (right), the sample after being subjected to the ageing procedure shows larger holes, due to the reduced cohesion between pigments, caused by the loss of binder. Note that superficial binder is not necessarily degraded to the same extend as binder on the inside of the sample.
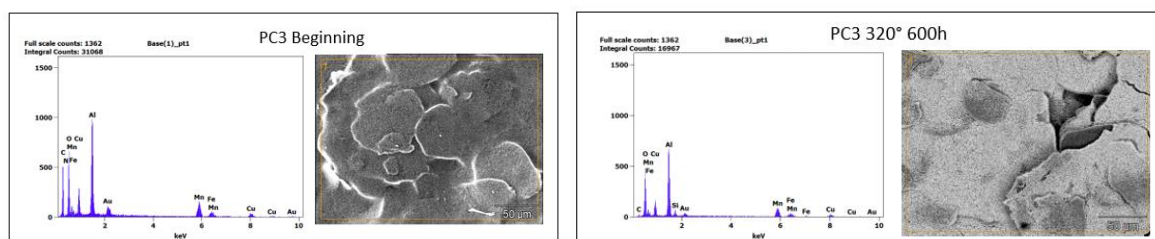
Figure 22 - EDS spectrum of initial PC2 and PC3 320°C 600h

As shown in figures 23, the metallic flakes are mostly constituted by aluminium (Al), copper (Cu), and manganese (Mn), with traces of other metallic components. The EDS spectra of PC3 and PC3 320°C 600h confirmed the degradation of the coatings. The decreased concentration of carbon and the complete loss of nitrogen support the conclusion that the polymeric binder, which is mainly constituted by these elements, was mostly degraded during the ageing process.

Table 1 - SUMMARY OF THE RESULTS OBTAINED IN THIS WORKsummary of the results obtained in this work

		PC2 (TSSS – Polysiloxane)	**PC3** (TISS – Polyurethane)
FTIR-‑ATR		- Characteristic bands of the polysiloxane appear after ageing	- Characteristic bands of the polyurethane disappear after ageing
TGA	AIR	- Thermally stable until 50°C	- Thermally stable until 240°C
	N_2	- Before ageing have two mass losses (in total 9% mass loss) associated with loss of polymer - After ageing has one small mass loss (0,56%)	- Before ageing have two mass losses (in total 30% mass loss) associated with loss of polymer - After ageing there was no mass loss
SEM		- Similar characteristics - Space between pigments less filled after ageing	- After ageing the metallic flakes were more exposed – less polyurethane
Optical Properties		↑Absorptance ↓Emittance Pc < 0.05	↑Absorptance ↓Emittance Pc < 0.05

13 CONCLUSIONS AND FUTURE PERSPECTIVES

Two types of spectrally selective paint coatings were studied, one based on polyurethane (PC3) and the other based on polysiloxane (PC2). The study of the changes in the structure of the coatings after ageing tests with temperature is done because it is one of the factors that alters the durability of the paints and thereby changes the efficiency of the collector.

FTIR spectroscopic analyses of the binder allowed the identification of the polymer that constitutes the coatings. In PC2 it was identified characteristic bands of polysiloxane. In PC3, the spectrum had characteristic bands of polyurethane. However, it was also identified characteristic bands of poly(styrene acrylate ester). For this work, and given that the manufacturer specifies the binder as polyurethane, it was considered the binder's polymer.

In both coatings, the thermal stability was evaluated based on the thermogram of the TGA test carried out in air and we obtained thermal stability up to higher temperature for PC3 (240°C) than for PC2 (50°C). To evaluate the composition of the coatings before and after being exposed to the thermal test, nitrogen TGA was performed. In PC2 after aging, it was still possible to identify a loss of mass - associated with the binder, so that during aging, the polymer that constitutes the binder remained in the composition. However, in the case of PC3, after aging, there was no mass loss, evidencing the degradation that occurred in the polymer during the thermal test.

SEM images of PC2 before and after ageing show similar characteristics, being possible to identify the spherical pigments. The main difference after the ageing process was that the space between pigments was less filled, evidencing a slight loss of polymer. The PC3 SEM images show the metallic flakes with the binder polymer. After the ageing process, these metallic flakes were more exposed creating a finer structure with less cohesion between pigments. This loss of cohesion is explained by the loss of polymer in the ageing process.

Globally, the optical properties of the coatings (absorptance and thermal emittance) improved when comparing their values at the beginning of the ageing process with the value at the end. Ignoring some experimental errors in the results, both coatings' absorptance evolutions are characterized by a steep initial increase, followed by a smooth and constant decrease. In contrast, the thermal emittance for both paints decreases abruptly at the beginning of the ageing process, slowly increasing thereafter. This leads to an evolution of the performance criteria with similar behaviour to the thermal emittance evolution: steep initial decrease, followed by a progressive increase. Even though the coatings have different degradation behaviours, as concluded by the FTIR, SEM, and TGA studies, they are qualified to be used as absorber coatings, according to their optical properties (absorptance and thermal emittance). This conclusion is attained from the results presented in figure 7, which clearly show that the performance criterion is always below the established value of 0.05.

As future perspectives, it is necessary to study these paints for higher temperature applications, since there are solar thermal collectors with a temperature range up to 500°C . To do so, tests at higher temperature (up to 500°C) have be performed to assess the thermal stability of PC2 and PC3.

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15 ANNEX

● ● ● ● ● **HELIOS** GROUP

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E info@helios.si
www.helios.si

SUNCOLOR PUR
2K polyurethane spectral selective coating

PRODUCT DESCRIPTION

- **SUNCOLOR PUR** independent of the thickness spectrally selective polyurethane coat, pigmented with high absorbtion and low emission pigments, with good optical characteristics, which enable effective use of sun energy
- Selectivity of coating does not depend on surface and may be applied to metal and nonmetal surfaces, it can be used as top coat or can be applied directly to surface
- Thermic emitance; 0.3-0.4 (depending on colour shade and application conditions)
- Sun absorbance; up to 0.91 (black, depending on application conditions),lower for other colour shades

USE

The coat is used for glazed roof solar collectors, glazed and not glazed facade collectors. The production of different colour shades is possible, which enables different architectural solutions further to known black collectors.

BELONGING COMPONENTS

Thinner: SUNCOLOR thinner
Hardener - comp. B: SUNCOLOR PUR comp.B

PRODUCT DATA

Type	acrylic polyol-isocyanate
Delivery viscosity components A	Tixotropic
Pot life A+B at 20°C	4 hours
Mixing ratio A:B	
By volume	17:1
By weight	20:1
Density components A	1.3 kg/l
Density A+B in delivery form	1.3 kg/l
Colour shades	black according to RAL card or sample
Appearance	matt
Solid substance	
By volume	37 %
By weight	61 %
VOC for A+B in delivery form	500 g/l
Temperature resistance (dry temperature)	
Short-term	up to 200 °C
Long-term	up to 160 °C

Coat thicknesses and coverage	Maximum	Recommended
Dry film thickness	80 µm	55 µm
Wet film thickness	220 µm	150 µm
Theoretical coverage	4,0 m²/l	7,0 m²/l

Drying			
Powder dry	4 hours	3 hours	2 hours
Dry to touch	10 hour	8 hour	6 hour
Dried through	10 days	7 days	3 days

Forced drying	
Flash-off	15 minutes
Drying	at 60-80°C: 15 minutes

Remarks: Drying times are stated with regard to recommended coat thickness and at suitable ventilation.

Responsible Care®
OUR COMMITMENT TO SUSTAINABILITY

ISO 9001
ISO 14001
BUREAU VERITAS
Certification

BUREAU VERITAS
1828

SURFACE PREPARATION

All surfaces should be clean, dry and free from grease. We recommend to treat surfaces and evaluate according to standard EN ISO 8504.
For pre-treatment of cold rolled steel we recommend phosphating.

WORKING CONDITIONS

Minimal temperature at the application: + 5°C.
Surface temperature should be at least 3°C over dew point.

APPLICATION

The coating should be thoroughly mixed before use.

AIR SPRAYING

Thinning:	up to 25 % by volume
Nozzle diameter:	1,0 - 1,0 mm
Exit pressure:	0,0 - 0,0 MPa

COATING SYSTEMS

Coat systems are selected with regard to type of climatic influences acc. to recommendations of standard EN ISO 12944-5.

For the application of other topcoats consult HELIOS experts.

STORAGE

12 months at the temperature from +5°C to +25°C, in the originally closed packaging.

SAFETY INSTRUCTIONS

See Material Safety Data Sheet and the product's label.

REMARKS

For each paint batch we issue a suitable quality certificate. Technical information is the result of knowledge, based on laboratory work and practical experience. In case of use of the coat beyond our control we can not assume the responsibility and only guarantee the quality of the coat itself. We reserve the right to change the data without previous notice. The quality system is in accordance with EN ISO 9001.

SOLKOTE HI/SORB-II™
Selective Solar Coating

SOLKOTE HI/SORB-II™ is an optical coating specifically formulated for solar thermal applications. Its high temperature tolerance, resistance to moisture and UV degradation, and excellent optical qualities make it an ideal, low cost substitute for electro or vacuum deposited selective surfaces. Its high absorptivity and strong adhesion to cementitious surfaces also make it an ideal passive coating. With a proven history of reliability and longevity, SOLKOTE has powered many of the world's largest solar thermal manufacturers' collectors since 1980. Is your collector Powered By SOLKOTE?

CHARACTERISTICS:
Thickness and substrate dependent. Low emissivity substrates, such as aluminum and copper, yield best optical properties. Emissivity can range from 0.20 to 0.49 depending on dry film thickness, substrate and surface preparation. Absorptivity will range from 0.88 to 0.94. Wet film thickness of 0.8 to 1.0 mils (0.020 to 0.025mm) and careful cleaning of substrate will yield optimum results.

Thermally tolerant from -100°F to +1000°F (-73°C to +538°C). High temperature adhesion is dependent upon careful substrate preparation and cure. No out-gassing when correctly cured. Resists UV and moisture degradation. Not recommended for immersion or unglazed applications.

USES:
All low to high temperature glazed active thermal applications including concentrating collectors. Most glazed passive thermal applications.

SUBSTRATES:
May be applied to aluminum, copper, steel, brick, stone, masonry, adobe and some plastics. Primers may be required for mild steel and galvanized surfaces. Primers will increase emissivity but will not affect absorptivity. Absorptivity is extremely high on cementitious or ceramic substrates but selectivity is moderate.

PHYSICAL AND CHEMICAL PROPERTIES:
Binder: 100% silicone polymer
Storage Temperature: -50°F to +80°F (-45°C to +27°C)
Odor Characteristics: Aromatic Hydrocarbon
Viscosity: 25 seconds #1 Zahn's Cup
Specific Gravity: (H2O=1) <1
% Solids by Weight: 15%
Shelf Life: 1 year from date of manufacture

Solvent: Xylene
Appearance: Very Dark Liquid
% Volatile by volume: 83%
Vapor Density: (Air=1) >1
Odor Threshold: 100 ppm
VOC Regulatory: 812 g/L, VOC Actual: 812 g/L

Hand-held spray application

DEGRADATION:
Unaffected by moisture, UV or elevated temperatures in glazed solar applications when correctly cured.

COVERAGE:
400 to 900 ft²/gallon (40-90 m²) at 1 mil wet film. Coverage will vary depending on application conditions.

MIXING:
SOLKOTE HI/SORB-II is supplied ready for use. No thinning is required or suggested. Mix well before using. Do not allow pigments to settle. If possible, agitate frequently during application.

OUTGASSING:
None when correctly cured.

Automated spray application

SURFACE PREPARATION:
Substrate preparation is extremely important since collectors are expected to function without maintenance for twenty years. Initial substrate emissivity and coating adhesion can be significantly improved through careful attention to surface preparation. SOLKOTE exhibits excellent adhesion on many substrates with little or no surface preparation. However, the following procedures are suggested to ensure the excellent optical properties and long-term durability available from this product.

Metallic Substrates:
Degrease metallic substrates using Xylene, Toluene, Acetone or other suitable solvents. This is generally considered minimum surface preparation. Copper, aluminum and stainless steel may also be lightly acid etched to remove surface oxides and lower emissivity. Aluminum may also be conversion coated to lessen future oxidation. Mild steel and galvanized surfaces should not be acid cleaned but may require priming. Use of primers will increase emissivity and may also raise absorptivity.

Passive Substrates:
Masonry substrates for passive application should be air cured for at least one month prior to application of SOLKOTE. Surface should be free of all paint, loose grout and dust. SOLKOTE has a natural affinity for most masonry substrates and ceramic surfaces, but is extremely thin. Suitable primers or fillers may be used to extend coverage. SOLKOTE will yield a highly absorptive and long-lived surface on cementitious substrates, but selectivity will be limited.

APPLICATION METHODS:

SOLKOTE has been formulated specifically for air atomization spray application. Simple spray guns normally used in automotive body repair facilities have proven to be quite adequate for application. Electrostatic and HVLP equipment is also suitable but substantially more expensive. Gun pressures should be kept fairly low (25-35 PSI) to lessen over spray and allow good thickness control. Remote pressure supply pots should have air driven agitators and the coating should be mixed as often as is practical during application. A wet film thickness of 0.8 to 1.0 mils (0.020 to 0.025mm) is ideal and may be easily measured using a wet film thickness gauge during application. Handheld airless equipment is not recommended, however specialized automated airless spray equipment may be utilized. Consult factory for questions with spray equipment selection. Substrate temperatures should not exceed 90°F (32°C) during application and surface should be dry prior to application. Good ventilation and operator protection is imperative.

DRYING AND CURE:

Curing is highly dependent upon substrate type, humidity and ambient temperature. Skin forms within 2 to 5 minutes; coated absorber may be normally handled after 1 to 3 hours drying at room temperature. SOLKOTE will naturally cure, to a point where no out-gassing will occur, within 3 days at room temperature of 60°F (16°C) or above. Curing may be easily accelerated by baking the coated absorber panel at temperatures ranging from 225°F (107°C) to 450°F (232°C) for a period of 15 minutes to one hour. Copper should not be cured at temperatures above 400°F (204°C) as it will oxidize and cause a decrease in coating adhesion. Other metals, such as aluminum and stainless steel, may be cured at temperatures up to 450°F (232°C). Coated absorber plates may also be placed in bright sunlight to accelerate curing. Hardness will increase with time and temperature. Experimentation will determine the best curing procedures for your particular environment.

CLEAN UP:

Clean spray gun and spray gun lines with Xylene.

STORAGE:

Store at room temperature with cap tightly sealed on container. Keep out of direct sunlight to avoid pressure increase in container. Best if used within 1 year of date of manufacture. Partial pails can be re-used after opening if stored properly and mixed thoroughly.

FIRST AID:

Eye Contact: Flush eyes with fresh water for at least 15 minutes.
Skin Contact: Clean exposed area with Isopropyl Alcohol, then wash with soap & water. If irritation occurs, get medical attention.
Inhalation: If shortness of breath occurs, remove person to fresh air. Administer oxygen if necessary.
Ingestion: Get medical attention immediately. DO NOT induce vomiting.

MIT/STG Int'l concentrating collector in Lesotho, southern Africa.

CAUTIONS:

CONTAINS flammable solvents.
DO NOT expose to elevated heat or open flames.
DO NOT take internally. Contains compounds that may be harmful.
AVOID breathing vapors or spray mist; wear respirator and apply in well-ventilated area.

DO NOT reuse container & do not transfer to bottles or other unmarked containers.
KEEP container closed when not in use. Close container after each use.
AVOID contact with eyes and skin.
DO NOT mix with other paints or thinners.

After using product, thoroughly wash hands with soap and water before eating, drinking or smoking.

KEEP OUT OF REACH OF CHILDREN

OSHA regulations, sections 1915.24 Painting, 1915.25 Flammable Liquids and 1915.82 Respiratory Protection give additional helpful safety suggestions. Review MSDS for more product information.

PACKAGING:

Available in 1 gallon and 5 gallon steel pails
1 gallons (3.785 liters) – 8.0 lbs (3.64 Kg)
5 gallons (18.925 Liters) – 42.0 lbs (19.09 Kg)

Unparalelled Proven Durability for the Life of Your Collector

1981 Gulf Thermal KYSM40, photographed 11/3/09. No deterioration of SOLKOTE surface after 28+ years of in-field use.

TRANSPORTATION INFORMATION:

Flammable liquid n.o.s. (Contains Xylene), Class 3, UN1993, PGIII
(All packaging is certified for air and ocean freight and available for export)

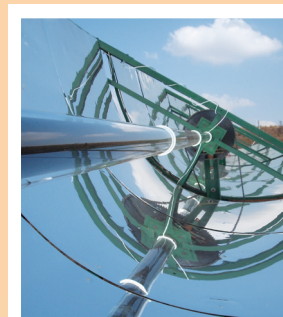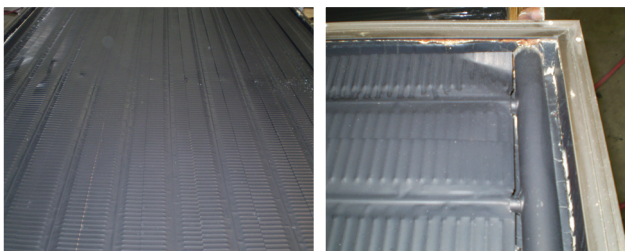## IMPORTANT NOTICE TO PURCHASER:

This bulletin is an introductory summary of SOLKOTE HI/SORB-II Selective Coating. The information provided is based upon typical installation conditions and tests we believe to be reliable. However, due to a wide variety of possible uses and conditions, SOLEC does not guarantee that typical values expressed will be necessarily obtained.

Seller's only obligation shall be to replace such quantity of the product proved to be defective. Seller shall not be liable for any injury, loss or damage, direct or consequential, arising out of the use of or inability to use the product. Before using, user shall determine the suitability of the product for their intended use, and user assumes all risk and liability whatsoever in connection therewith. No statement or recommendation shall have any force or effect unless in an agreement signed by officers of seller and user.

RESEARCH FACILITIES:

SOLEC-Solar Energy Corp. maintains a complete laboratory for the analysis of selective solar coatings. Equipment includes a surface emissometer, solar spectrum reflectometer and alphasometer, Bausch & Lomb metallurgical microscopes, twelve-sun natural light accelerated coating tester, accelerated coating UV and moisture system, high temperature thermal cycling systems, and data logging and computer equipment necessary for coating research. Our low cost services for the analysis of selective surfaces are used by many of the world's largest solar manufacturers. Please contact us for prices.

Contact factory for SOLKOTE pricing and any additional technical questions.

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