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Chemical Degradation and Color Changes of Paint Protective Coatings Used in Solar Glass Mirrors

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Abstract: This paper reports a study of the influence of outdoor natural aging on paint coatings applied to the back of three commercial solar glass mirrors (A1, C2, and D2) under two different exposure environments (marine and desert) in Morocco for a period of about three years. The aging assessment was carried out through colorimetric measurements and FTIR-ATR (Attenuated total reflection-Fourier transform infrared) analyses of the top coat paints. The obtained results demonstrate that the tested coating system had a high resistance at the desert site. Under the desert environment, no obvious changes to the coating occurred after 350 days. However, at the marine site, some color changes were detected, and the coating got yellow and more matte, especially for mirror A1. FTIR-ATR analyses have indicated many modifications in the intensity of many bonds of infrared spectra especially for paint of this mirror type (A1). This chemical degradation is not only due to UV degradation but also related to many factors, such as humidity, salinity, and rainfall. This finding was concluded after the faster degradation observed on samples exposed at the marine site. The present study confirms the need to use different exposure environments for testing the limits of new protective systems for solar glass mirrors rather than using only the real service conditions. Finally, accelerated tests are necessary for understanding the effect of each degrading parameter and their results should be compared to outdoor tests data for a complete analysis of coatings durability.

Keywords: paint aging; solar mirrors; chemical degradation; color change

1. Introduction

Today, concentrating solar power (CSP) is became the major source of renewable electricity generation in Morocco. The country has implemented the world’s largest concentrated solar farm in Ouarzazate city that will provide 580 megawatts and save the planet from over 760,000 tons of carbon emissions [1]. Morocco has one of the best solar regimes in the world with an average direct insulation of 2200 kWh·m−2·year−1 and a wide range of climates (desert and arid areas). It has one of most ambitious energy targets in the world. The goal is for 52% of its power to come from renewable sources (20% solar, 20% wind, 12% hydro) by 2030 [1–3]. The country is well on track to hit its target, too, with 35% of its energy being already renewable thanks to sites such as Noor Ouarzazate, Noor Midelt and Noor Boujdour.

Moroccan research institutions must support these industrial challenges through the launch of several research programs in order to contribute to CSP technology development, market deployment, and energy partnerships for sustainable, reliable, efficient, and cost-competitive concentrating solar technologies. Moreover, those research programs should
provide information and recommendations to policy-makers. Within this context, MASCIR (Moroccan Foundation for Advanced Science, Innovation and Research) has launched in collaboration with CEA (Commissariat à l’Énergie Atomique et aux Énergies Alternatives, France) a study that has as main objective testing the durability of solar mirrors used for CSP plants under different Moroccan weather conditions [4–10].

In the last decade, scientists have been endeavoring to develop new materials for solar technologies with ideal performances for CSP plants [11–17]. The conducted studies have yielded important technical improvements which help to increase the overall efficiency of CSP technologies. However, more improvements are needed in order to achieve a large portion of the world’s demand for electricity. Reflectors (mirrors) are the major components of the solar field in all CSP technologies (parabolic trough, solar power tower, linear Fresnel, and dish Stirling). Since the solar field accounts for nearly half the total plant construction cost, optical performances and durability of reflectors are paramount. The reflector cost for all CSP technologies represents about 30% of the collector cost. Mirrors reflect and focus the sunlight onto a receiver to create high-temperature steam to drive conventional steam turbines. Thus, optical performance of mirrors used should ensure high efficiency and stability over the lifetime of the CSP plant, which is required to be at least 25 years [11].

Monolithic glass mirrors are the main technology used as solar reflectors in CSP power plants. This technology consists of a 1–4 mm low iron glass layer coated with a reflective silver layer which is protected with a layer of copper and a protective paint system composed by several coatings on the mirrors back. The role of these coatings is to protect the metallic layers against corrosion by creating a barrier to the diffusion of contaminants present in the atmosphere to the metallic layers [18]. The paint material used in monolithic mirrors consists of two (thin mirrors) or three (thick mirrors) protective coatings. The primer and intermediate layers contain zinc, magnesium, calcium, barium, sulfur, iron, silicon, and lead in oxide, sulphate, or borate states. The prime layer acts as a corrosion preventer and the intermediate layer as a diffusion barrier. The top coat contains a polymeric binder and stabilizers, such as TiO₂ (rutile) and ZnO, which prevent UV radiation from reaching the intermediate paint layer [15]. Paint coatings for exterior applications are made up of four compound types: Binder, fillers, solvents, and additives [19–21]. The binder is the main part of paint coatings. The binder is mainly responsible for adhesion with the substrate. In most cases, it is a macromolecular organic compound [20,21]. Binders for mirrored paint coatings are commonly based on poly acrylates, melamine, urethane, and epoxy bases. Fillers influence the physical properties of the coating, its appearance and its resistance to corrosion. The main used pigments are titanium dioxide (TiO₂) and iron oxides (FeO or Fe₂O₃). The first is a white pigment used in exterior coatings and provides good UV protection thanks to its high refractive index. The second is found in a wide variety of forms, has a red color, and can be contained in both primer and top layers. Other inorganic pigments are used to modify paint density, permeability, flow, and hardness. The three most common are calcium carbonates (CaCO₃), silicates like talc (Mg₃Si₄O₁₀(OH)₂), and barium sulfate (BaSO₄). Solvents, usually organic, are used to modulate the viscosity of the binder in order to apply more easily the coating to the substrate with conventional methods. Solvents evaporate when the coating crosslinks [19]. Additives are chemical compounds that are added in small amounts to modify the properties of the paint systems.

Many coating systems were developed and tested by solar mirror manufacturers in order to provide new solar reflectors with less paint layer thickness and enhanced lifetime [22].

Paint coatings, as well as other layers composed monolithic glass mirrors, are subject to physico-chemical degradation when exposed to natural environments. The most common chemical mechanisms leading to degradation of coatings are photochemical degradation and hydrolysis resulting from UV radiation, air, and water [20,21]. These processes can sometimes work together, such that the overall rate of degradation is greater than the sum of the individual components. Those degradation mechanisms are thermally-activated processes, whose rate increases with exposure temperature. Hydrolytic degradation maybe
enhanced by exposure to acid, from acid rain or from acids that reside in the coating, for example, acid catalysts used to enhance the rate of cross-linking. Other atmospheric degrading factors, such as ozone and oxides of nitrogen and sulfur, play a minor role compared to photo-oxidation and hydrolysis [20,21].

The severity of degradation is related to the aggressivity of exposure environments. The degradation of paint films alters their protective role and causes corrosion of reflective layer and, therefore, decreases the lifetime of solar mirrors. Depending to their application, several factors could influence the durability of paints, such as temperature, solar irradiation, humidity, pollution, and moisture [23,24]. The resistance of paint coatings to environmental stress is usually evaluated in term of changes in physical properties or appearance. Thus, paint system weatherability is assessed in terms of embrittlement and cracking, loss of adhesion, loss of gloss, and color change, while corrosion protection is assessed in terms of paint blistering, loss of paint adhesion, and pitting or perforation of the substrate.

Accelerated tests, such as salt-spray test, wet/dry cycle corrosion tests, and a combination of corrosion/weathering tests, and wet/dry corrosion cycles with ultraviolet (UV) condensation cycles, allow evaluating paint resistance under extreme conditions and permit understanding of the effect of each degrading parameter on paint behavior [20,25]. These tests are based on correlation of the physical changes induced by the selected test exposure conditions with those observed under some standard conditions (e.g., a defined course of natural exposure). However, analyzing the synergic effect of degradations resulting from all/or some combinations of the degrading factors (temperature, UV irradiation, humidity, salinity, pollution, and moisture) is only possible by using outdoor exposure tests. To achieve a better understanding of the real behavior of paint coatings, indoor tests results should be compared and validated by outdoor testing data.

This paper presents the results of outdoor exposure tests of paint coating applied to the backs of three commercial solar glass mirrors exposed under two different climates (marine and desert) in Morocco.

2. Materials and Methods

2.1. Paints

Three types of commercial monolithic silvered-glass from manufacturers 1 and 2 with different glass thicknesses (two thick mirrors (A1 and C2) and one thin sample (D2)) have been subject to weathering tests on two different exposure sites in Morocco (marine and desert sites). The description and the detailed composition of each mirror have been given in a previous publication [6]. Tested mirrors were cut from larger mirrors supplied by manufacturers with at least one protected edge. Samples were tested as received without any initial laboratory preparations. The initial colorimetric $L^*a^*b^*$G and XYZ values of the outer paint coating of each mirror are given in Table 1.

| Sample | CIE Lab Space | XYZ Space |
|--------|---------------|-----------|
|        | $L^*$ | $a^*$ | $b^*$ | $G$ | $X$ | $Y$ | $Z$ |
| A1     | 93.50 | −1.30 | −0.90 | 38 | 79.50 | 84.30 | 92.90 |
| C2     | 94.59 | −0.85 | −0.04 | 43 | 81.93 | 86.66 | 94.41 |
| D2     | 95.49 | −0.98 | 0.47  | 46 | 83.87 | 88.78 | 95.96 |

The paints applied on monolithic mirrors tested in this study use organic binders composed of a mixture of alkyd resin, acrylic copolymer, styrene, and a melamine resin (HMMM). The pigments composing these paints can be found in Table 2 according to XRD analysis conducted on the un-exposed samples of each mirror type [6].
Table 2. Description of paint systems used in each tested mirror.

| Mirror | Paint Coatings System | Paint Thickness (µm) | Pigments                        |
|--------|------------------------|----------------------|---------------------------------|
| A1     | 3                      | 90                   | TiO$_2$, BaSO$_4$, and Mg$_3$Si$_4$O$_{10}$ |
| C2     | 3                      | 90                   | TiO$_2$, BaSO$_4$, and Mg$_3$Si$_4$O$_{10}$ |
| D2     | 2                      | 64                   | TiO$_2$, BaSO$_4$, and Mg$_3$Si$_4$O$_{10}$ |

2.2. Outdoor Exposure Tests

In this study, paints were subject to natural weathering using two different outdoor testing sites in Morocco which are located respectively in Temara and Skoura (Table 1). Both sites were equipped with meteorological stations enabling high-frequency measurements of various parameters. Temperature, relative humidity, wind speed and direction, total solar irradiation, UVA/UVB irradiation, IR irradiation, and rainfall measurements are recorded every 10 s. Mirrors facing the sun were exposed, at an angle equal to the latitude of exposure site, in racks enabling placing two different mirror sizes: 7 × 7 cm$^2$ and 20 × 20 cm$^2$. Different frequencies were used for site visits conducted to characterize aged samples: 7, 15, 30, and 60 days. After each exposure period, samples were cleaned with deionized water during site visits.

2.2.1. Exposure in Temara

Mirrors were exposed at 32$^\circ$ to the horizontal for 24 months in the seaside site. The exposure start date and total exposure time of each sample used in this study is given in Table 3.

Table 3. Exposure start date and exposure time for mirrors tested at the seaside site.

| Mirror Sample | Exposure Start Date | Exposure Time (Days) |
|---------------|---------------------|----------------------|
| A1-12         | 11 October 2012     | 77                   |
| A1-13         | 11 October 2012     | 77                   |
| A1-14         | 11 October 2012     | 250                  |
| A1-15         | 11 October 2012     | 250                  |
| A1-18         | 11 October 2012     | 416                  |
| A1-19         | 11 October 2012     | 416                  |
| A1-20         | 11 October 2012     | 615                  |
| C2-2          | 27 March 2013       | 541                  |
| C2-9          | 25 July 2013        | 423                  |
| C2-10         | 25 July 2013        | 478                  |
| C2-11         | 25 July 2013        | 442                  |
| C2-12         | 25 July 2013        | 427                  |
| D2-2          | 27 July 2013        | 541                  |
| D2-9          | 25 July 2013        | 423                  |
| D2-10         | 25 July 2013        | 478                  |
| D2-11         | 25 July 2013        | 442                  |
| D2-12         | 25 July 2013        | 427                  |

The seaside site is located in Temara on the Atlantic shore near Rabat city (Northern Morocco, Figure 1). This site has a very aggressive humid and salty weather together with strong winds during the different seasons of the year. It is situated very close to a cliff; samples are then subjected to a very important saline mist [6]. The monthly average climatic parameters of Temara site are given in Table 4.

Table 4. Mean, minimum, and maximum values of weather conditions during exposure period time at the seaside site.

| Value   | Air Temperature °C | Total Irradiation (kWh/m²) | Relative Humidity (%) | Daily Rainfall (mm) | Wind Speed (m/s) |
|---------|---------------------|----------------------------|-----------------------|---------------------|------------------|
| Mean    | 17.7                | 5.4                        | 81.2                  | 1.5                 | 2.47             |
| Maximum | 32.1                | 8.8                        | 99.7                  | 53.4                | 2.82             |
| Minimum | 5.7                 | 0.6                        | 33.5                  | 0                   | 1.85             |
2.2.2. Exposure in Skoura

Mirrors were exposed at $45^\circ$ to the horizontal for 22 months. Meteorological parameters for this exposure site are presented in Table 5.

Table 5. Mean, minimum, and maximum values of weather conditions during exposure period time at the desert site.

| Value   | Air Temperature $^\circ$C | Total Irradiation (kWh/m$^2$) | Relative Humidity (%) | Daily Rainfall (mm) | Wind Speed (m/s) |
|---------|---------------------------|-------------------------------|-----------------------|---------------------|------------------|
| Mean    | 17.8                      | 5.9                           | 30.1                  | 0.36                | 1.67             |
| Maximum | 32.7                      | 7.9                           | 99.3                  | 64.3                | 17.66            |
| Minimum | 5.7                       | 0.6                           | 1.8                   | 0                   | 0.94             |

Two exposure periods were used: 30 and 60 days. The exposure start dates and total exposure time of all tested samples are summarized in Table 6.

2.3. Analysis of Mirrors Degradation

Other analytical techniques were performed on tested mirrors in order to characterize and follow the mirrors degradation during exposure time. Every site visit, mirrors are controlled on exposure sites by measuring their specular reflectance before and after cleaning. This allows measuring the reflectivity loss due to the mirrors aging. Reflectance is measured for all samples using a portable spectrophotometer model 15R (Devices and Services, Dallas, TX, USA) which allows measuring the specular reflectance at 660 nm with $15^\circ$ incidence angle and 12.5 mrad acceptance angle in the center of the sample at three to five different points. Mirrors are cleaned using deionized water and optical wet paper to remove adhered soils. Finally, cleaned samples are wiped with a dry optical paper. Every three months the surface degradations of aged mirrors are characterized in laboratory
by a Nikon LV150 optical microscope (Nikon Instruments Europe BV, Amsterdam, The Netherlands). The results of these analyses are discussed in a previous publication [6,23].

Table 6. Exposure start date and exposure time for mirrors tested at the desert site.

| Mirror Sample | Exposure Start Date | Exposure Time (Days) |
|---------------|---------------------|----------------------|
| A1-2          | 30 April 2013       | 664                  |
| A1-3          | 30 April 2013       | 664                  |
| A1-5          | 30 April 2013       | 664                  |
| A1-8          | 27 August 2013      | 545                  |
| A1-9          | 27 August 2013      | 545                  |
| C2-5          | 30 April 2013       | 664                  |
| C2-6          | 30 April 2013       | 419                  |
| C2-7          | 30 April 2013       | 664                  |
| C2-8          | 30 April 2013       | 664                  |
| C2-13         | 27 August 2013      | 545                  |
| C2-14         | 27 August 2013      | 545                  |
| D2-5          | 30 April 2013       | 664                  |
| D2-6          | 30 April 2013       | 421                  |
| D2-7          | 30 April 2013       | 664                  |
| D2-8          | 30 April 2013       | 664                  |
| D2-13         | 27 August 2013      | 545                  |

2.4. Color Measurements

Color measurements were carried out using portable colorimeter from BYK (spectro-guide 45°/0° gloss) which allow measuring color in two different spaces (CIE L*a*b*, CIE XYZ). The (CIE L*a*b*) space is the most commonly used. This system uses three spatial coordinates to define color. The L parameter represents the brightness (L = 0 corresponds to black, L = 100 corresponds to white), while a and b are the color-opponent dimensions: a is the red/green balance (negative values corresponds to green and positive values corresponds to red), and b is the yellow/blue balance (negative values corresponds to blue and positive values corresponds to yellow) [26].

The overall color difference (ΔE) was calculated for each sample using Equation (1) [27]:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$  \hspace{1cm} (1)

where ΔL, Δa and Δb are differences in the respective values before and after aging. The variation of gloss parameter (ΔG) was calculated for each sample using Equation (2):

$$\Delta G = G(t) - G(0)$$  \hspace{1cm} (2)

where G(0) and G(t) correspond to the average gloss values calculated, respectively, before exposure tests and after each exposure time (t) during aging tests.

CIE XYZ space allows measuring yellowness (Yi) of paint calculated according to the ASTM standard E313 method [28]. The following equation is used:

$$Y_i = \frac{100(C_x X - C_z Z)}{Y}$$  \hspace{1cm} (3)

where X, Y, and Z are the space coordinates on the CIE XYZ space, and Cx and Cz are constants.

Six measurements were performed on each sample at different locations. The average value was calculated and reported in this paper. The measurements were taken directly on the back of the mirrors to measure the color parameters of the upper layer (white layer) [6]. Three measurements were performed on different locations on the back of each sample.
2.5. ATR-FTIR Spectroscopy Analysis

FTIR (Fourier transform infrared) spectroscopy analyses were performed employing a spectrometer Spectrum 400 from Perkin Elmer (Buckinghamshire, UK) equipped with an attenuated total reflection accessory (ATR). The resolution was set at 4 cm\(^{-1}\), 64 scans were recorded for each analysis, and the scanning range was from 650 to 4000 cm\(^{-1}\). FTIR-ATR analyses of aged paint samples were conducted in order to follow paint structure modification during aging time. For this reason, we have compared infrared spectra of aged paints with the unexposed paint spectrum for each mirror type. This comparison was carried out by monitoring the evolution of peaks ratio during time. For this reason, all spectra have been normalized by the absorption band of the C–O–C vibration at 1010 cm\(^{-1}\). Three specimens were analyzed per mirror type.

3. Results
3.1. FTIR-ATR

In order to characterize the aging of the chemical structure of tested paints, infrared spectroscopy was performed on samples before and after exposure. Spectra of non-exposed and exposed samples are presented in Figures 2–4.

![Figure 2. FTIR-ATR paint spectra of (a) mirror A1, (b) mirror C2, and (c) mirror D2, exposed on both outdoor testing sites (Seaside and desert sites).](image-url)
Many changes were observed on Mirror type A1 after exposure at both sites. Concerning mirrors C2 and D2, no significant differences were detected between samples analyzed before and after exposure, except the absorption bands at 3650–3100 cm\(^{-1}\) and 2926–2855 cm\(^{-1}\). Table 7 lists the main functional groups and pigments of paint samples.

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**Figure 3.** Windows of FTIR-ATR spectra of mirror A1 paint samples before and after exposure at the seaside site. (a) 3500–2500 cm\(^{-1}\); (b) 1800–1500 cm\(^{-1}\); (c) 1580–1400 cm\(^{-1}\); (d) 1400–1050 cm\(^{-1}\).

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**Figure 4.** Windows of FTIR-ATR spectra of mirror A1 paint samples before and after exposure at the desert site. (a) 3500–2500 cm\(^{-1}\); (b) 1800–1500 cm\(^{-1}\); (c) 1580–1400 cm\(^{-1}\); (d) 1400–1050 cm\(^{-1}\).
Many changes were observed on Mirror type A1 after exposure at both sites. Concerning mirrors C2 and D2, no significant differences were detected between samples analyzed before and after exposure, except the absorption bands at $3650–3100 \text{ cm}^{-1}$ and $2926–2855 \text{ cm}^{-1}$. Table 7 lists the main functional groups and pigments of paint samples.

Table 7. FTIR-ATR infrared absorption of white paint used in tested mirrors.

| Wavenumber (cm$^{-1}$) | Functional Groups and Pigments |
|------------------------|--------------------------------|
| 3800–3250              | O–H; N–H                      |
| 2962–2872              | C–H Stretching (CH$_3$)        |
| 2926–2853              | C–H Stretching (CH$_2$)        |
| 1720                   | C=O stretching of the esters   |
| 1507–1489              | C=C stretching of the polybasic acid |
| 1450                   | C–H asymmetric stretching (CH$_3$) |
| 1420                   | C=O stretching sym (CO$_3$– from CaCO$_3$) |
| 1381                   | C–H Symetric (CH$_3$)          |
| 1240                   | C–O Stretching (arylesters)    |
| 1174                   | v( C–O) of ester (cottonseed oil), TiO$_2$ et BaSO$_4$ vibration |
| 1119                   | v(C–O) of O–CH$_2$ (phthalate) and BaSO$_4$ vibration |
| 1070–1038              | in plane deformation of aromatic CH and BaSO$_4$ vibration |
| 1016                   | C–O-C, TiO$_2$, SiO$_2$ Stretching |

By considering the following infrared regions, it is possible to describe the chemical modifications observed on paint structure for tested mirrors [22,29,30]:

- **O–H and N–H stretching (3650–3100 cm$^{-1}$):** An increase of the relative intensity in this region was observed on infrared spectra of mirror 2 samples after 314 exposure days. Changes in this infrared region may be interpreted as a partial depolymerization of the organic matrix’s structure. These latter bonds may be assigned to the symmetric and asymmetric stretching vibrations of N–H links in secondary or in primary (amine functions and/or to the characteristic vibrations of the O–H hydroxyl groups [29]. The formation of amino and/or hydroxyl functional groups suggested that the degradation reactions occurred at the level where the resins crosslink. The crosslinking of the paint is achieved with the HMMM resin and forms ether links with the alkyd resin. This could be explained by the degradation mechanism proposed by in which paint degradation occurred in two steps: The first step consists of a hydrolysis reaction of the ether links in order to form terminal hydroxyl groups on the alkyd resin and methyol groups (–CH$_2$–OH) on the melamine resin; during the second step, the methyol groups previously formed may then hydrolyze giving way to primary and secondary amine functions.

- **C–H stretching (2926 and 2855 cm$^{-1}$):** A decrease of the infrared region at 2926 and 2855 cm$^{-1}$ can be noticed for mirror A1 exposed at Temara site after 416 days. The methylene groups of the paint binder were prone to diminish possibly due to the oxidation of double bonds which is shown by a gradual decrease in absorption in the asymmetric and symmetric (C–H) CH$_2$ stretching at this region.

- **C=O stretching (1750–1700 cm$^{-1}$):** A decrease was observed on the carbonyl stretching absorption at 1720 cm$^{-1}$, for mirror A1 exposed at Temara and Skoura site after 554 and 314 days, respectively. This modification could due to thermal oxidation of the binder during aging [22,30].

- **C=C of aromatic ring (1650–1450 cm$^{-1}$):** The peak centered at 1507 cm$^{-1}$ attributed to the aromatic stretching of the C=C bond of the polybasic acid part of the alkyd binder, was no longer present in infrared spectra of mirror A1 exposed at Temara and Skoura site after 557 and 314 days, respectively. This is probably due to the scission of the polymeric chain of the paint binder caused by UV aging of paint samples at both sites.

- **(1254–1070 cm$^{-1}$):** A slight decrease in the intensity of the peaks at this infrared region was noticed for Mirrors A1 exposed at Temara site. This infrared region is attributed to several bond vibrations of both phases (organic binder and mineral pigments).
composing the white paints of monolithic mirrors. The absorption bands of the binder and pigments (in particular TiO₂, CaCO₃, and BaSO₄) overlap in this region.

For example, the absorption peak of CaCO₃ at 1420 cm⁻¹ is hidden by the asymmetric elongation band of the C-H bond. Similarly, the C–O bonds of the polymeric binder hide the absorption bands of BaSO₄ pigments at 1174 and 119 cm⁻¹. In addition, these pigments are also hidden by two peaks corresponding to the aromatic vibrations C–H at 1070 and 1038 cm⁻¹. Thus, the changes at this region could be due to pigments degradation at this humid site.

3.2. Colorimetric Measurements

The color measurement results of all tested paints exposed at both sites are summarized in Figures 5–9, which include the gloss change (ΔG), total color change (ΔE), redness/greenness (Δa*), yellowness/blueness (Δb*), and the yellowing (ΔYi).

**Figure 5.** Evolution of gloss variation (ΔG) of monolithic mirrors A1, C2, and D2 paint coatings during exposure time at (a) the seaside site and (b) desert site.

**Figure 6.** Evolution of total color change (ΔE) of monolithic mirrors A1, C2, and D2 paint coatings during exposure time at (a) the seaside site and (b) desert site.
Figure 7. Evolution of color parameters ($\Delta a$ and $\Delta b$) of monolithic mirrors (a) A1, (b) C2, and (c) D2 paint coatings during exposure time at the seaside site.
Figure 8. Evolution of color parameters (Δa and Δb) of monolithic mirrors (a) A1, (b) C2, and (c) D2 paint coatings during exposure time at the desert site.

The gloss change (ΔG) during aging at both exposure sites is presented in Figure 5. For the desert site, the tested samples in general preserved their original gloss after 300 days. An intriguing fact is that a moderately increasing trend was observed dependent on the mirror’s type. For the seaside site, an important increasing trend of gloss was observed for mirrors C2 and D2, especially after 350 days. In the case of mirror A1, the gloss change was totally different. The initial increase during the first 100 days was followed by a decrease until 170 days, and then the trend increased again for the majority of exposed samples. For the most exposed sample (A1–20), an important decrease in gloss was observed after 450 days. This gloss evolution of mirror A1 may be due to moisture content in samples fluctuating after each exposure period of time at this very humid site.

The obtained curves for total color change (ΔE) show an increase during time for paint samples exposed at the seaside site compared to a small variation for paint samples exposed at the desert site. The higher the ΔE is, the higher the overall color modification of paint coatings. For samples exposed at the desert site, the ΔE values were lower and stable around 0.5. Concerning paint samples exposed at the seaside site, paint of mirror 2 (C2 and D2) have presented more color stability than paints of mirrors type 1 (A1) after more than 350 exposure days, with discoloration values of 1 and 2, respectively.

The analysis of Δa and Δb variation shows a clear correlation between total color change (ΔE) and total yellowness/blueness (Δb) variation (Figures 7 and 8). According to Figure 7, Δa has tended to remain stable throughout the entire duration of the exposure test while Δb has shown a similar variation during time than ΔE for the three paints. The Δb increase is an indicator of a color shift from white to yellow in the CIE Lab color space. This indicates a yellowing of the top coating paint of monolithic mirrors during aging time at the seaside site. Moreover, Figure 7 shows that Δb variation was more important for mirror A1, which explains the significant total color change observed on this mirrors type compared to mirrors C2 and D2.
Figure 8. Evolution of color parameters (Δa and Δb) of monolithic mirrors (a) A1, (b) C2, and (c) D2 paint coatings during exposure time at the desert site.

Figure 9. Evolution of yellowing parameter (ΔYi) of monolithic mirrors (a) A1, (b) C2, and (c) D2 paint coatings for samples exposed at the seaside site (left) and the desert site (right).

The yellowing parameter (Yi) measurements results confirm this latter result. As can be seen from Figure 9, this parameter, calculated in CIE XYZ color space, presents a similar variation during time than both parameters (ΔE and Δb) of CIE Lab space. This confirms that color change observed on the monolithic mirrors top paints is due to yellowing of white paint coatings and it is more significant for mirrors A1. This result agrees with the FTIR-ATR results. Indeed, yellowing is a paint discoloration which could result from different chemical degradation mechanisms of paints: photodegradation, binder degradation, degradation of additives, and the presence of impurities [21,31–35]. The chemical degradation of paints during exposure leads to changes in the physical appearance and performance of the top coating (color change, gloss loss, cracking, peeling, or chalking) and, thus, impacts the protective properties of other paint layers as well as the metallic layers. Contaminants (UV, H₂O, O₂, salts, etc.) presented at exposure sites could then penetrate through aged paint coatings and cause metallic layer corrosion [6].

Paint coatings, as well as other layers composed monolithic glass mirrors, are subject to physico-chemical degradation when exposed to natural environments. The severity of degradation is related to the aggressivity of exposure environments. The degradation of paint films alters their protective role and causes corrosion of reflective layer and, therefore, decreases the lifetime of solar mirrors. Many parameters influence the durability of paints,
such as temperature, humidity, and solar irradiation. Photodegradation is the main factor causing surface degradation of paint. For this reason, modifications due to exposures were compared using the UV dose received by paint samples during aging time. Figure 10 shows the yellowing ($\Delta Y_i$) values of tested paints in terms of two kinds of abscissa: cumulative total UV radiation (kWh·m$^{-2}$) and the exposure time in days. Total UV radiation corresponds here to the summation of the different regions of the electromagnetic spectrum, such as the UV, visible, and infrared radiation.

![Figure 10](image.png)

**Figure 10.** Evolution of yellowing parameter ($\Delta Y_i$) in function of (a) cumulative solar radiation and (b) exposure time of monolithic mirrors (A1, C2 and D2) paint coatings exposed at the seaside site (left) and the desert site (right).

When analyzing the different curves, it appears that each exposure site has a different impact on the paint and, each paint responds differently. From this figure, it is clearly seen that marine site has causing the most pronounced degradation in terms of yellowness for all tested samples. Moreover, this figure shows that Paint A1 was the most sensitive paint in the marine site and the more resistant paint in the desert one. Since both sites are characterized by very different climates and tested paint have not been exposed in the same period, this finding suggests that degradation cannot be compared simply in terms of the UV or quantity of energy samples receive or the length of time they are exposed to the weather; there are other factors than photo degradation that modify color of paints such as marine salts, erosion and high humidity, etc.
4. Overview and Recommendations

The outdoor tests parameters and the main results obtained from characterizing the aged paints in both exposure sites are summarized in Table 8. The use of these data will give solar mirrors manufacturers relevant information about the real behavior of paint in desert and marine environmental climates. This will help them to develop best practices for durability testing of solar components and also to choose the most reliable technology of protective paint coatings depending to service conditions of glass mirrors. According to the experimental results of this study, the successful performance of all paints at the desert site, which is characterized by higher irradiation and temperature, indicates that tested paints have high resistance to photo degradation.

| Site   | Paint | Lat. Long          | Total Solar Radiation (kWh/m²) | Av. Temperature (min/max) °C | Av. Relative Humidity (%) | Rain (mm) | Exposure Time (Day) | Aging of Binder Chemical Structure | Max Color Variation (ΔE/ΔY) |
|--------|-------|--------------------|--------------------------------|-----------------------------|---------------------------|-----------|--------------------|-----------------------------------|-------------------------------|
| Temara | A1    | 33.90° N 6.96° W   | 25,758                         | 5.9/29.8                    | 81.2                      | 764       | 615                | Many changes in FTIR-ATR spectra | 1.6/4.7                       |
|        | C2    | 9950               | 5.9/29.8                       | 81.2                        | 373                       | 495       |                    | Only O–H stretching              | 0.8/1.7                       |
|        | D2    | 9950               | 5.9/29.8                       | 81.2                        | 373                       | 495       |                    | -                                 | 0.7/1.0                       |
| Skoura | A1    | 30.94° N 6.93° W   | 7570                           | −1.7/40.1                   | 26.5                      | 301       | 664                | Many changes in FTIR-ATR spectra | −2.4/1.1                      |
|        | C2    | 4277               | 5/40.1                         | 21.3                        | 301                       | 340       |                    | Only O–H stretching              | 0.3/1.6                       |
|        | D2    | 4277               | 5/40.1                         | 21.3                        | 301                       | 340       |                    | -                                 | −0.7/2.0                      |

For this reason, desert and dry environments could be used to test the resistance of paint against UV radiation. In other hand, the higher rate of degradation in the marine site, characterized by high humidity and salinity, suggests that such extreme environments should be used in order to accelerate the degradation of new developed paints during natural exposure. This will help manufactures to have faster results about paint behavior under natural exposure. As consequence, they will have the possibility to make necessary modifications to their new products after shorter testing time than when using real service conditions or other exposure environments. Additionally, such environments will allow testing the synergic effect of photo degradation and degradation resulting from humidity, salinity, moisture, and rain on paint durability.

Finally, the effect of each climatic and environmental parameter on paint degradation cannot be sufficient analyzed under outdoor exposure. Accelerated exposure tests are important to provide complementary results and also to have an indication of the long-term durability of paints in their end use environment.

5. Conclusions

This work investigates the influence of natural aging on chemical structure and color change of top coatings applied on the back of three types of commercial glass mirrors exposed in two different climate conditions in Morocco (Temara and Skoura). The results of colorimetric measurements showed that the coating system used in tested glass mirrors was high resistant to the environmental conditions of the desert site. At this site, there were no obvious changes of paint color and gloss. Under the marine site, certain changes were present for paint samples of mirrors A1: The coatings turned somewhat yellow under the aggressive environmental and meteorological conditions (UV radiation, humidity,
salinity) and they also showed very moderate gloss degradation after 450 days. Paint samples of mirrors C2 and D2 showed better color stability compared to mirror A1. The characterization of aged samples has indicated chemical modifications during aging of the organic binder especially for samples exposed at the marine site. The comparison made on different samples at both exposure sites have shown that paint yellowing cannot be only correlated to the accumulated UV quantity received by exposed samples nor the test period but to other parameters such as humidity, salinity, and rainfall. Finally, the signs of degradation observed on paint samples at the marine site indicate that such environments could be used to test the durability of glass mirrors paints in a shorter time.

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