

## **SYNTHETIC WHITE PIGMENTS (WHITE TITANIUM AND WHITE ZINC) IN DIFFERENT BINDING MEDIA. INFLUENCE OF ENVIRONMENTAL AGENTS**

### **ABSTRACT**

This work concerns the behaviour of white pigments of white titanium and white zinc in different media both of natural and synthetic binders. In addition, a study was made of the impact that time, high-energy UV radiation, warming by infrared radiation, or saturation processes of relative humidity exert on stability and chromaticity of the preparations. The composition of pigments and binders as well as the time course of their preparations were studied by X-ray diffraction, mass spectrometry, electron microscopy, and instrumental colour measurement. The effect of the passage of time, UV, and infrared exposure together with moisture saturation were found to result in losses in elasticity and cracking of the film generated by the binder, the latter two factors causing the most severe losses. The greatest variations were detected in the colorimetric study, reflecting the utility of instrumental colour measurements for these types of studies. The chromatic variations detected consist fundamentally of loss in luminosity ( $\Delta L$ ) and chroma ( $\Delta C$ ) as well as a slight yellowing tendency. In general, the preparations based on natural binders were more affected than those based on synthetic products.

**KEY WORDS:** Titanium white pigment; Zinc white pigment; Physical properties, Weathering, Durability.

### **1. INTRODUCTION**

The use of pigments in different applications within the field of Engineering, the science of the materials and intervention in architectonic heritage, is necessary in many cases to achieve a certain exterior appearance<sup>1</sup>, as well as to undertake actions requiring matching visual and aesthetic characteristics, but also to improve, for example photovoltaic light-capturing efficiency<sup>3</sup>, the cover capacity of ceramic enamels in construction<sup>4,5</sup>, and acrylic photoprotective coatings<sup>6</sup>, while lowering resource consumption<sup>7,8</sup>, cost, environmental impact<sup>4,9,10</sup>, etc.

Specifically, the pigments titanium oxide and zinc oxide are frequently used in different materials and media that come from natural or artificial raw materials<sup>11, 12, 13</sup> with a broad range of compositions and various proportions of pigments together with different media needed for their application and composition. Many factors during the production of these mixtures affect the quality and the technical features, such as the type of pigment, the binder, the composition, etc., both in the manufacturing industry of these materials, as well as in the use of the mixtures in their different applications.

It is fundamental to know the performance of these pigments in different media and guarantee greater suitability and durability of their effectiveness as well as their characteristics and finishes<sup>14,15</sup>, as these are determinant in architectonic materials and designs as well as in restoration<sup>16</sup>. Also of special importance is the need to ascertain the effect both of the passage of time (aging) as well as of the exposure to environmental agents, UV rays, warming, and humidity.

Technically, many studies and manufacturers have investigated the features of the pigments, the characteristics of organic as well as inorganic pigments, which have focused primarily on the production processes and their formulation, the most suitable application methods that preserve the environment, resource savings, and product finish. However, their performance and effectiveness differ depending on the media and exposure conditions. Therefore, these materials need to be studied over time in relation to the needs they are meant to serve.

In the present work, we focus on one of the applications mentioned, specifically the one related to the field of restoration of cultural heritage and architectonic interventions. In this sense, we examine the intended use for the pigments studied, the suitability of their physical characteristics, and the features of the materials, and we investigate their colorimetric implications.

The function of pigments is fundamental in the preparation of the chromatic palette as well as throughout the execution of artwork. Today, white pigments are used in the field of art, decoration, building, industry, serving as bases, preparation, coatings, and protections on all types of surfaces, this requiring resistance, durability, and stability. In addition to their use in white colour, these pigments are essential in mixtures to achieve specific tones, corrections, glazes, carnation, etc.. Thus, these are essential components in any pictorial manifestation and therefore their nature and performance need to be ascertained not only to broaden knowledge or analyse diverse pictorial media, but also to control possible restoration/conservation techniques. In this respect, it is important to understand their reaction with the passage of time as well as the effect of environmental agents such as the exposure to given levels of ultraviolet radiation, rises in temperature, or variations in relative humidity, as demonstrated elsewhere<sup>17,18,19,20,21,22,23,24,25,26,27</sup>. The general behaviour of pigments has been established in some pictorial media according to the physical-chemical features of the material. Recent works have applied instrumental colour study in the field of monumental heritage, as in monitoring stone restoration<sup>28,29</sup>, as well as in analysing the performance of pigments treated with restoration products<sup>30,31, 32,33,34,35,36</sup>.

To determine the main factors that influence the characteristics of the material, we used different experimental techniques. The performance of the pigments  $O_2Ti$  and  $OZn$  were characterized in various organic and inorganic binders, by X-ray diffraction (XRD), scanning electron microscopy (SEM), and mass spectrometry (ICP?), in an effort to recognize the structural changes and development of new mineral phases, while chromatic performance was assessed by diffuse spectral-reflectance measurements. Also, the influence on these pictorial preparations exerted by passage of time and such environmental factors as ultraviolet light, temperature, and high humidity were studied. The media selected included binders and solvents belonging to classical media (linseed oil, poppyseed oil, mastic varnish, etc.) as well as new synthetic products (resins, vinyl emulsions, ...), enabling a comparison between the old and new techniques.

On the other hand, both pigments were selected according to their stability, their widespread use, and their ease of handling. Nevertheless, except for certain characteristics, they present optimal properties to be mixed with fatty or lean binders. Resistant to solvents and to alkali, these are appropriate for use in different applications and especially in interior as well as exterior elements.

The colour-difference values (total colour  $\Delta E$ , luminosity  $\Delta L$ , chroma  $\Delta C$ , and hue  $\Delta H$ ) between the mixture and the pure pigment in each of the media studied identified which of them offered greater effectiveness and stability and indicated their chromatic specifications (higher or lower degree of luminosity and chroma, possible variation of hue, etc.); but, above all, it provided a quantitative evaluation of the influence of the environment on the medium, with respect to the final visual result.

## **2. MATERIALS AND METHODS**

Two inorganic pigments were studied: titanium white (Colour Index Name PW 6 and Colour Index Number 77891) and zinc white (Colour Index Name PW 4 and Colour Index Number 77947). (Table 1).

With respect to the titanium white used in this work, the results of the XRD analysis (Figure 1) indicated that this was a polymorphous anatase synthetic, of chemical composition  $O_2Ti$ , of great purity<sup>37</sup>. It has an excellent lightfastness rating and permanency, with high opacity (high covering power); a tint strength of 42.25 and a gloss average of 43.15. Its refraction index is 2.72<sup>38,39</sup>.

With regard to zinc white, the results of the same XRD analysis showed that this was zincite synthetic, of chemical composition  $OZn$  and of equally great purity<sup>37</sup>. It also has an excellent lightfastness rating and permanency with high transparency (low opacity or low covering power), a tint strength of 27.20 and a Gloss Average of 58.87. Its refraction index is 2.08<sup>38</sup>.

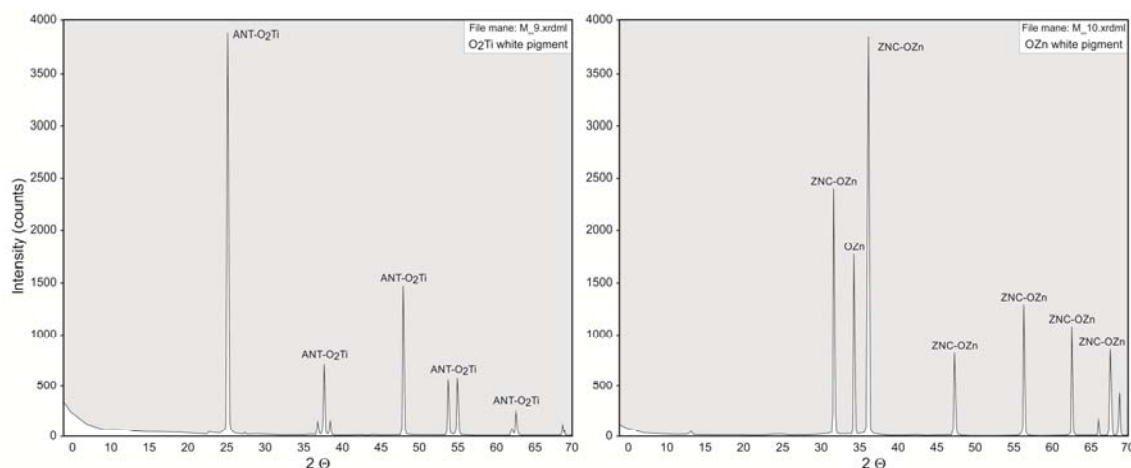


Figure 1. XRD diffractograms of the pigments studied: TiO<sub>2</sub> white pigment and ZnO white pigment.

Pigment colour	Colour index name/number	Permanency 1(excellent) 5(poor)	Transparency/Opacity 1 (less opaque) 8 (most opaque)	Chemical description crystal system	Lightfastness 1(excellent) 5(poor)	Tint strength	Gloss average	Refraction index	Density g/cm <sup>3</sup>
Titanium white	PW-4/77891	1	6	Anatase synthetic O <sub>2</sub> Ti Tetragonal	1	42.25	43.15	2.72	4.06
Zinc white	PW-6/77947	1	3	Zincite synthetic OZn Hexagonal	1	27.20	58.87	2.08	5.61

Table 1. Main properties of the white pigments used in this study, in accordance with<sup>40,41,42,43</sup>

With respect to the different binders, 11 were selected, some classically used and others recently introduced, (oil, varnish, tempera, encaustic, watercolour, or gouache). Table 1 lists these most frequently used media and corresponding binders and solvents, grouped as natural or synthetic.

Initial	Binder (composition)	Solvent (composition)	Technical artistic application
AD	Poppyseed oil (oleic, linoleic, and palmitic acids)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Oil painting
ALM	Mastic and Venetian turpentine (terpenic hydrocarbons and mastic resin)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Varnish
D	Dammar resin (triterpenic resin)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Varnish
LC	Crude linseed oil (linoleic acid)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Oil painting
LP	Polymerized linseed oil (Linoleic acid)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Oil painting
LTV	Linseed oil and Venetian turpentine (linoleic acid+terpenic hydrocarbons)	Turpentine and White spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Varnish
EN	White wax (stearic acid)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Encaustic

ENR	White wax and Dammar resin (stearic acid+resin triterpenic)	Turpentine and white spirit (terpenic hydrocarbons + aliphatic, alicyclic and aromatic hydrocarbons)	Encaustic
MWD	Vinyl emulsion Mowilith DMC-2F (ethylene vinyl acetate copolymer)	Distilled water	Vinyl water synthetic tempera
MWR	Vinyl resin Mowilith 35/73 (F) (copolymer of vinyl acetate and dibutyl maleate)	Turpentine and nitro cellulose solvent (terpenic hydrocarbons + aromatic hydrocarbons and ketone solvents)	Vinyl solvent synthetic tempera
PAV	Polyvinyl alcohol Rhodorsil (Moviol) 4/125 (polyvinyl alcohol)	Distilled water	Water synthetic tempera

Table 2. List of current and classical binders with indication, where appropriate, of trademark, solvent, chemical composition and most commonly applied painting technique<sup>21,24,44</sup> grouped as natural or synthetic.

A total of 144 samples were taken (72 per pigment) and subdivided into 3 groups corresponding to the 3 aging assays to which the samples were subsequently submitted.

Each preparation contained the following proportions: 1 g of pigment, 2 ml of binder, and 2 ml of solvent. The pigments were ground in an agate mortar together with the binder and solvent after appropriate homogenization of the supports.

A problem to solve was to find the appropriate support on which to spread the mixtures to form the pictorial layer and identify which would provide adequate absorption of the products, a reasonable drying time, and a rigid and stable surface without specular components (e.g. glass or plastic would be undesirable for spectrophotometric measurement). In agreement with previous work<sup>19</sup>, we finally applied the preparations to small plaster plaques which were white of high purity, brightness, and quality. In this sense, the material selected presented a whiteness index of more than 80% and a minimum chromatic variation on its surface<sup>28</sup>. The plaster plaques used had adequate surface hardness, flatness, and constant overall porosity. The plaster supports used had the following characteristics (Table 3):

Uniaxial compression resistance (Mpa)	Fire classification	Surface density (kg./m <sup>2</sup> )	Flatness mm/mm	Resistance against flexotractor (Mpa)	Surface hardness. Shore	Total porosity (%)	Whiteness index (%)
> 3.43	A1	9.5-9.92	< 0.85/1000	0.07 - 0.1	75	27 - 30	> 85

Table 3. Main properties of plaster plaques according to other sources<sup>45,46,47</sup>.

The different mixtures, previously prepared, were applied to the plaster support with a flat paintbrush (n° 5) of natural sable, making a total of 4 coats. Strokes were applied in criss-cross to avoid possible discolouring, irregularities, and other defects in the final result. The mixtures on the plaster plaques were

dried and hardened under controlled conditions of moisture and temperature (23 °C – 60% HR), for 20 days before the colorimetric measurement.

Three aging assays were conducted using the plaques in order to ascertain their subsequent impact in the recognition tests. Specifically, these were natural aging, ultraviolet light (UVA AGING), and infrared radiation together with hydration (INFRARED-HEATING AND H<sub>2</sub>O AGING).

In relation to the natural-aging test, 24 samples were stored for 12 months under the following conditions of drying, exposure, and maintenance: specifically HR 50-55%, with a possible variation of +/-5%; temperature 18°C with possible fluctuations of +/-2 degrees; Lux: maximum chroma of 50 lux.

To control the incidence of ultraviolet radiation, we exposed the preparations (24 samples) to 500 h of high-energy UV radiation in an environmental aging chamber, MARCA QUV ACCELERATED WEATHERING TESTER with a radiation interval from 280 to 400 nm.

Similarly, 24 samples of specific mixtures were placed in a convection oven at 100°C for 50 h in a high-temperature oven with forced-air circulation for temperatures from 60 to 400 °C, with a resolution of 1°C. Afterwards, these samples were kept one month in a humidity-saturated environment, in a glass-drying hood containing distilled water, at room temperature controlled to 23°C.

The X-ray diffraction samples were analysed using a Bruker D8 Advance diffractometer with 2-theta geometry, a Lynxeye copper and radiation detector, from the Scientific Instruments Centre (CIC) of the University of Granada. The compounds were determined with the program Xpolder<sup>49</sup>, which takes into account multiple iterations of models of mixture for better accuracy with the real diffractogram. The error is the minimum that currently may occur for the interpretation by XRD. According to technical specifications of the diffractometer, minerals that can be detected should have a relative proportion in the sample increased to two percent. A total of 12 samples were measured.

The organic compounds and their possible transformations were determined with a Mass Spectrometer with a time-of-flight (TOF) Analyzer, and Triwave WATERS system, model SYNAP G2. Also a liquid chromatograph was used with ultra-high pressure, (UPLC) WATERS ACQUITY H CLASS model, both belonging to the CIC. A total of 12 samples were measured.

The electron microscopy studies used a scanning electron microscope of the CIC, model Hitachi S-510, with a voltage of acceleration of 25 kv, ranges increasing from 20x to 150,000x, 5 mm distance from work, detector EDX Röntec M Series, Edwin, Si (Li), and Edwin Röntec microanalysis system. A total of 12 samples were measured.

Regarding the colorimetric evaluation, a total of 144 samples were measured. After the samples were prepared (and after 20 days of drying), their diffuse spectral-reflectance curves were measured in the visible range using a Konica Minolta CM-2500c Spectrophotometer, which has a wavelength of 360 nm to 740 nm and observer 2/10 degrees (CIE 1931/2°, CIE 1964/10°), of the University of Granada (Spain). The measurement was made after sampling each 5 nm within the visible range over a sampling area of some 0.8 cm in diameter and observing a geometry of illumination/observation for each diffuse/2-10° sample, excluding the specular component of the reflection, as recommended in these cases by the CIE<sup>48</sup>. From these reflectance values, the CIE-1931 chromaticity coordinates were calculated under the D65 illuminant, as were the total colour-difference values ( $\Delta E$ ), luminosity ( $\Delta L$ ), chroma ( $\Delta C$ ), and hue ( $\Delta H$ ), according to the formulae CMC(2:1)<sup>50</sup> between the mixture and pure pigment in each of the media tested. Complementarily, the software Color Data Software SpectraMagic NX was used to present the simulations of the colour variations for the samples affected.

After exposure to the conditions established in the different aging assays, all the samples were measured by diffuse, spectral reflectance.

### **3. RESULTS AND DISCUSSION**

In the case of electron microscopy, the results proved more significant differences between the non-aged samples and the naturally aged ones (after polymerization) and the ones aged by infrared warming and saturated humidity (Figs. 2 and 3).

Visually, a pronounced textural change occurred in the samples aged naturally in comparison to the non-aged ones, with a greater increase in the samples subjected to infrared aging and saturated humidity. These textural changes developed generally from more smoothed and continuous textures towards cracked textures and fragile pictorial films. It can also be inferred that there was a loss of elasticity in the binding materials, which were altered in a natural or chosen way, as can be seen in the corresponding images. It is notable in some cases that after the aging assay, heat and saturated humidity caused the pictorial films to lose homogeneity, with binding remains appearing in the form of fine threads, especially in the case of the titanium white pigment and the raw binders polymerized linseed and poppyseed oil. In general, all of these textural changes exerted their effects on the total colour variations ( $\Delta E$ ) of the samples and, in particular, on declines in luminosity ( $\Delta L$ ) or darkening, as well as in progressive loss of chroma ( $\Delta C$ ) with extreme yellowing.

With respect to the compositional variations, measurements by EDX analysis reflected no changes, so that the inorganic compounds of Ti and Zn were the pigments that continued with the same presence in the naturally aged samples, those submitted to accelerated UV aging, and those subjected to heating and saturated humidity.

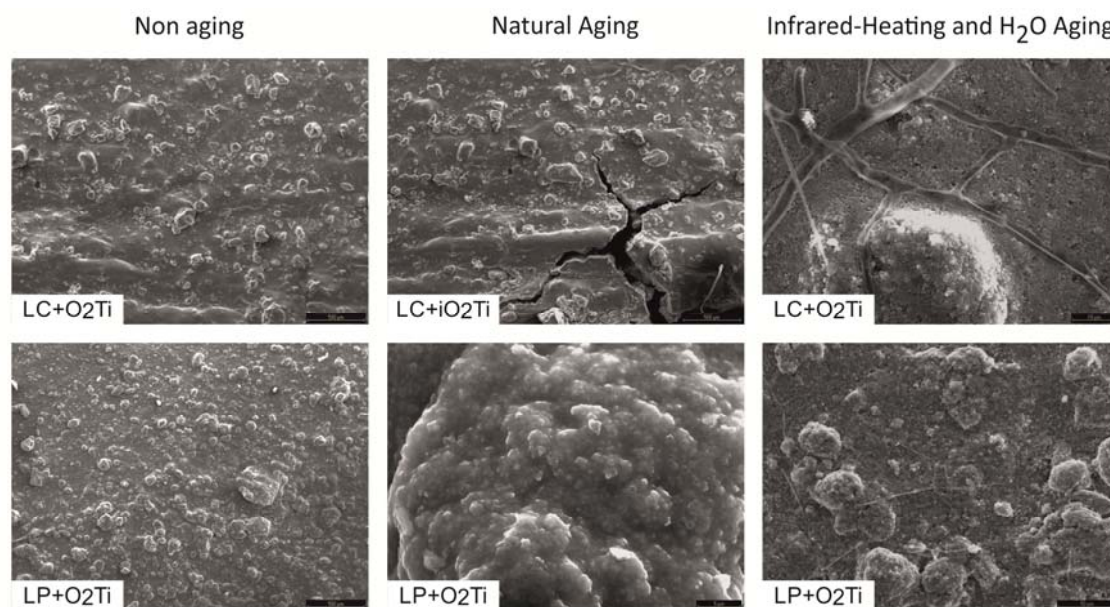


Figure 2. SEM images corresponding to textural variations in samples of binders with raw linseed oil (LC) and polymerized linseed oil (LP) and titanium white (O<sub>2</sub>Ti), not aged, naturally aged, and aged by heating and saturated relative humidity. From left to right appears less smooth textural variation, as well as the appearance of scattered binders in the form of fine threads. All of these changes provoked visual variations in total colour ( $\Delta E$ ), loss in luminosity ( $\Delta L$ ) and in chroma ( $\Delta C$ ), with the appearance of yellowing in the samples.



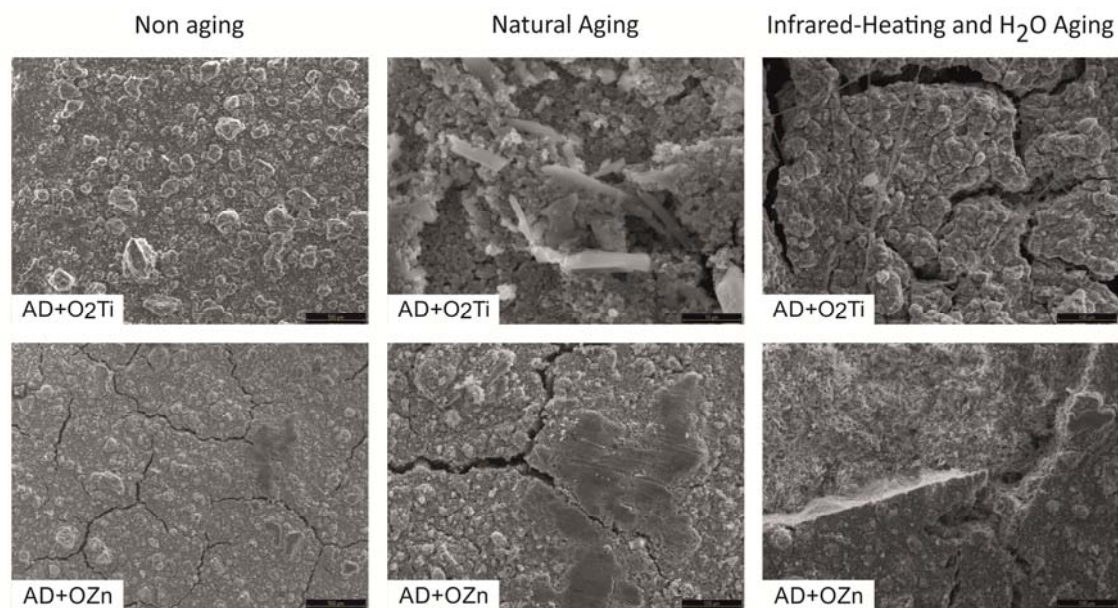


Figure 3. SEM images corresponding to textural variations of binder samples with poppyseed oil (AD) and titanium white ( $O_2Ti$ ) and zinc white ( $OZn$ ), respectively. The images show non-aged pictorial films, naturally aged ones and those aged by warming and saturated relative humidity. From left to right appears a less smooth textural variation, as well as the appearance of scattered binders in the form of fine threads and an increase in cracks and microfissures. The textural changes provoked visual variations in total colour ( $\Delta E$ ), loss of luminosity ( $\Delta L$ ), and loss of chroma ( $\Delta C$ ), with the appearance of yellowing in the samples.

The results of the mass-spectrometric study evidenced the high variability in the composition and the proportion of components in the samples analysed. Nevertheless, regardless of the high degree of difference between the components of each of the samples, a consistent change appeared in all cases due to the aging processes to which the samples were subjected.

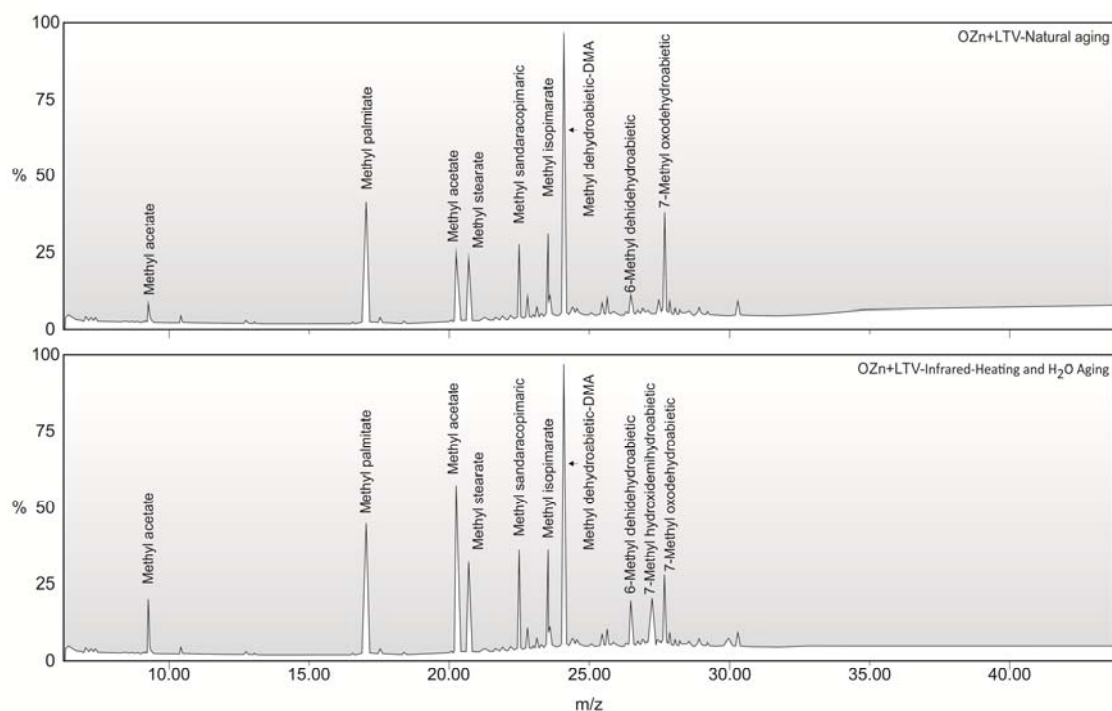


Figure 4. Spectrograms of the sample bearing linseed oil and Venetian turpentine (LTV) without being submitted to an assay of natural aging and after being submitted to infrared radiation and hydration, highlighting the main constituents and their transformation.

As shown in Figure 4 for the linseed-oil and the Venetian turpentine (LTV) sample, after a period of aging the methyl oleate degraded, diminishing in the sample subjected to the infrared radiation and hydration, due presumably to its polymerization. In the same way, methyl dehydroabietate was transformed by oxidation into methyl 7-oxodehydroabietate. It bears emphasizing that the changes in the structures of the compounds were minor. The rest of the samples offered very similar results and in all cases the changes were imperceptible.

Regarding the colorimetric analyses as the most decisive ones performed, and considering setting the value limit at 3 units necessary for the visual perception of absolute differences in the parameter Total Colour ( $\Delta E$ )<sup>49</sup>, we found different effects in the results grouped for each aging assay.

In relation to the pigments used, Table 4 shows that both pigments were so achromatic that they constituted almost perfect whites while the high value of the refraction indexes indicated high covering power.

Pigment	x	y	Y	L*	a*	b*
Titanium White	0.3142	0.3303	94.96	93.66	-1.71	3.21
Zinc White	0.3142	0.3315	90.90	90.04	-0.82	0.94

Table 4. Lists the pigments with the values of the CIE 1931 (x, y, Y) and CIELAB (L\*, a\*, b\*) chromatic coordinates.

With respect to the colorimetric results, during the aging assays, some samples were affected, undergoing damage on their surfaces (peeling and cracking), which impeded their measurement. Thus, some samples lack data for some samples in the corresponding tables. The effect was uneven for each type of aging, and it was noticeable that samples subjected to UV radiation registered the highest number of deteriorated samples.

### 3.1. NATURAL AGING

In the case of natural aging, the most significant effects appeared in the poppyseed with titanium oxide (AD+ O<sub>2</sub>Ti) samples in which the colour varied, reflected in a notable darkening of the mixture, with a visual change towards grey tones and a sharp increase in chroma or visual shift towards more orangish colours. The same binder in the case of zinc oxide did not give rise to appreciable variations for the human eye.

Also, mastic with titanium oxide (ALM+O<sub>2</sub>Ti) underwent visible colour variations, with notably greater chroma, a more solid colour with less transparency (orangish), as well as changes in hue, i.e. yellowing of the samples. The samples with zinc oxide (ALM+OZn) showed slighter variations, with darkening or changes towards greys in the mixture.

The sample of dammar and titanium oxide (D+ O<sub>2</sub>Ti) underwent a slight overall change consisting of a minor increase in chroma of the mixture or a tendency towards orangish colours. This was similar but more acute in the mixture based on zinc oxide (D+OZn).

The samples with encaustic (EN and ENR + O<sub>2</sub>Ti and OZn) showed no significant changes in any case.

On the contrary, in the samples with raw linseed oil and titanium oxide (LC+ O<sub>2</sub>Ti), pronounced colour variations resulted with strong darkening or a grey-black tendency and greater yellowing in the mixture. However, for zinc oxide (LC+OZn), no visual changes were perceptible to the human eye.

In the case of the binder polymerized linseed oil with titanium oxide (LP+ O<sub>2</sub>Ti) the colour changes affected luminosity, chroma, and hue, or, equivalently, a blackening and overall orangish coloration and yellowing of the mixture. Changes were slight or almost negligible in the case of zinc oxide LP+OZn).

The samples with linseed oil and Venetian turpentine with titanium oxide (LTV+TiO<sub>2</sub>) underwent a colour change as a strong increase in chroma or change towards orangish tones. With zinc oxide, in addition to the trend towards orangish colours, there was a darkening or blackening of the mixture.

The samples of Mowilith and Mowilith Resin (MWD and MWR) with both pigments (O<sub>2</sub>Ti and OZn) showed no effects on colour.

Finally, in the case of the mixtures of Polyvinyl Rhodorsil (PAV), the only effect detected was in the samples with zinc oxide, which showed a slight darkening or greyish shift of the samples.

In summary, as shown in Table 5, the values indicate the strong effect of natural aging on the titanium samples and more specifically on those called natural, where significant changes were found in the total colour (AE), somewhat less with respect to luminosity (AL), chroma (AC), and hue (AH). On the contrary, the synthetic samples hardly changed.

In the specific case of the zinc oxide samples, the effects were slighter in absolute values, with notably greater effects on the natural samples than on the synthetic ones, changes being perceptible fundamentally in the parameter total colour ( $\Delta E$ ), this being minimal in the rest of the parameters, for the case of luminosity and chroma, and absent in the case of hue.

Sample	$O_2Ti$								$OZn$							
	$\Delta E$	$\sigma$	$\Delta L$	$\sigma$	$\Delta C$	$\sigma$	$\Delta H$	$\sigma$	$\Delta E$	$\sigma$	$\Delta L$	$\sigma$	$\Delta C$	$\sigma$	$\Delta H$	$\sigma$
AD	<b>8.47</b>	0.20	<b>-3.44</b>	-0.10	<b>7.49</b>	0.10	-1.93	-0.01	2.66	0.04	1.19	0.03	2.38	0.05	0.07	0.00
ALM	<b>6.93</b>	0.16	-1.79	-0.04	<b>5.93</b>	0.14	<b>-3.12</b>	-0.06	<b>3.7</b>	0.09	<b>3.59</b>	0.09	0.88	0.02	0.24	0.01
D	<b>3.94</b>	0.09	-1.11	-0.02	<b>3.62</b>	0.04	-1.1	-0.02	<b>4.63</b>	0.11	-2.02	-0.05	<b>3.96</b>	0.10	-1.31	-0.03
LC	<b>7.52</b>	0.11	<b>-5.38</b>	-0.01	0.22	0.00	<b>-5.25</b>	-0.12	2.31	0.03	-0.73	-0.01	-1.71	-0.03	-1.38	-0.02
LP	<b>6.91</b>	0.15	<b>-4.13</b>	-0.02	<b>4.48</b>	0.09	<b>-3.25</b>	-0.07	<b>3.47</b>	0.07	-2.32	-0.07	2.53	0.05	-0.52	-0.01
LTV	<b>8.16</b>	0.14	-2.99	-0.09	<b>7.13</b>	0.03	-2.61	-0.06	<b>6.64</b>	0.16	<b>5.66</b>	0.11	<b>-3.46</b>	-0.08	0.12	0.00
EN	2.76	0.04	-2.18	-0.06	1.52	0.02	-0.75	-0.01								
ENR	1.79	0.03	-0.78	-0.02	1.32	0.02	-0.93	-0.03	0.77	0.01	0.67	0.00	-0.31	0.00	-0.21	0.00
MWD	1.36	0.02	0.71	0.01	-0.19	-0.01	-1.14	-0.03	0.7	0.01	0.56	0.01	0.09	0.00	0.42	0.01
MWR	1.1	0.03	0.01	0.00	0.62	0.01	0.91	0.01	2.23	0.04	-2.15	0.00	-0.6	-0.01	0.08	0.00
PAV	0.75	0.02	-0.64	-0.01	0.35	0.00	-0.18	0.00	<b>3.12</b>	0.07	<b>-3.01</b>	-0.01	0.68	0.02	-0.46	-0.01

Table 5. Mean values for differences in total colour ( $\Delta E$ ), luminosity ( $\Delta L$ ), chroma ( $\Delta C$ ), and hue ( $\Delta H$ ) among the pure pigments and each of the binders-media assayed in the D65 illuminant with natural aging.

### 3.2. UVA AGING

The aging test by UVA rays showed that the poppyseed sample with titanium oxide (AD+  $O_2Ti$ ) substantially changed colour, with a decided greying to a minor degree with a strong increase in chroma or a bias towards orangish colours, as well as yellowing, also to a minor degree. For the zinc oxide samples, the variations were not appreciable to the human eye.

In the case of mastic and titanium oxide (ALM+  $O_2Ti$ ), the variations were slight, more determined by the increased chroma or shifts towards orangish tones in the mixture. The same was true of zinc oxide (ALM+ $OZn$ ), although the effect was stronger.

The encaustic sample with titanium oxide (EN+  $O_2Ti$ ) blackened and turned orangish. The sample with zinc oxide (EN+ $OZn$ ) could not be measured because of deterioration.

The changes in the samples of encaustic and resin with titanium oxide (ENR+  $O_2Ti$ ) greyed and turned orangish, the most relevant changes being chroma shifts to orangish tones in the mixtures with zinc oxide (ENR+ $OZn$ ).

Together with the poppyseed samples, the mixtures of raw linseed and titanium oxide (LC+ O<sub>2</sub>Ti) presented the most pronounced colour variations in the aging assay, darkening and following a tendency towards grey-black, with an increasing yellowing in the mixture. The zinc oxide (LC+OZn) sample showed no changes perceptible to the human eye.

The colour change of the linseed and Venetian turpentine samples with titanium oxide (LTV+ O<sub>2</sub>Ti) tended towards greying, a sharp increase in chroma or a change towards orangish tones, with a predominance of yellowing. With zinc oxide (LTV+OZn), certain colours increased in chroma or became orangish.

The samples of Mowilith and Mowilith resin (MWD and MWR) with both pigments (O<sub>2</sub>Ti and OZn) showed no colour change.

The effect remains unknown with this type of assay on the samples of polyvinyl Rhodorsil (PAV+ O<sub>2</sub>Ti) and polymerized linseed (LP) and dammar (D) with the two pigments, as the mixture was lost from the support and therefore could not be measured.

Table 6 presents the total colour differences ( $\Delta E$ ), luminosity ( $\Delta L$ ), chroma ( $\Delta C$ ), and hue ( $\Delta H$ ) between the preparations before and after the exposure to UV radiation.

In the case of the titanium samples, the effect of the different parameters was greater than in the previous case, becoming highly significant in the case of the natural samples as opposed to the synthetic ones. The increase in total colour proved substantial, with a less marked decrease in luminosity, an increase in chroma, and a weaker increase in hue.

As with natural aging, the response of the zinc samples by UVA radiation was weaker, affecting only the natural samples with little or no effect, as in the case of total colour variation with values close to 3.

Sample	O <sub>2</sub> Ti								OZn							
	$\Delta E$	$\sigma$	$\Delta L$	$\sigma$	$\Delta C$	$\sigma$	$\Delta H$	$\sigma$	$\Delta E$	$\sigma$	$\Delta L$	$\sigma$	$\Delta C$	$\sigma$	$\Delta H$	$\sigma$
AD	<b>12.03</b>	0.35	<b>-4.77</b>	-0.10	<b>10.53</b>	0.23	<b>-3.33</b>	-0.03	2.89	0.06	0.41	0.01	2.81	0.05	-0.53	0.00
ALM	<b>3.82</b>	0.08	-1.45	-0.03	2.86	0.08	-2.09	-0.04	<b>3.27</b>	0.06	-1.13	-0.03	<b>3.05</b>	0.05	-0.3	-0.01
D																
LC	<b>6.56</b>	0.02	<b>-4.04</b>	-0.10	-1.58	-0.03	<b>-4.92</b>	-0.12	2.27	0.01	-1.59	-0.04	-0.53	-0.01	-1.54	-0.03
LP																
LTV	<b>12.93</b>	0.37	<b>-5.23</b>	-0.14	<b>11.32</b>	0.31	<b>-3.43</b>	-0.08	<b>4.48</b>	0.09	-1.21	-0.04	<b>4.27</b>	0.03	-0.66	-0.01
EN	<b>9.23</b>	0.27	<b>-4.54</b>	-0.13	<b>7.8</b>	0.23	-1.91	-0.01								
ENR	<b>6.74</b>	0.13	<b>-4.64</b>	-0.09	<b>4.37</b>	0.09	-2.17	-0.01	<b>4.58</b>	0.05	-2.66	-0.05	<b>3.68</b>	0.03	-0.59	0.00
MWD	0.24	0.00	0.06	0.00	0.17	0.00	-0.16	0.00	0.87	0.03	-0.8	-0.02	0.27	0.00	-0.21	0.00
MWR	0.52	0.01	-0.16	0.00	0.12	0.00	-0.48	-0.01	0.51	0.01	-0.49	-0.01	-0.02	0.00	-0.16	0.00
PAV									1.14	0.02	-0.74	-0.02	0.83	0.02	-0.25	-0.01

Table 6. Mean values of differences in total colour ( $\Delta E$ ), luminosity( $\Delta L$ ), chroma ( $\Delta C$ ), and hue ( $\Delta H$ ) between pure pigments and each of the binders-media assayed under the D65 illuminant with UV aging.

### 3.3. INFRAREDS AND HUMIDITY

In the case of the aging assay accelerated by infrareds and saturation in water, there was a repeatedly strong effect on the samples of poppyseed and titanium oxide (AD+ O<sub>2</sub>Ti), resulting in a marked colour change, particularly blackening of the mixture and a notable increase in chroma and a trend towards orangish colours as well as yellowing. In the case of zinc oxide (AD+OZn), the mixture darkened and blackened, with increased chroma, shifts towards orangish colours, and to a lesser extent yellowing.

The samples of mastic and titanium oxide (ALM+ O<sub>2</sub>Ti) underwent greying and a strong change in chroma or changes to orangish tones in the mixture. The samples with zinc oxide (ALM+OZn) showed a greater increase in chroma or a shift towards orangish tones.

The dammar samples with titanium oxide (D+ O<sub>2</sub>Ti) slightly increased in chroma or turned orangish. Similar alterations were undergone by the zinc oxide (D+OZn) samples.

In the encaustic samples EN and ENR with titanium oxide (O<sub>2</sub>Ti), the changes were slighter or negligible, being more pronounced for the increase in chroma or changes towards orangish tones. In the zinc oxide (OZn) samples the changes were practically null.

The mixtures of raw linseed oil and titanium oxide (LC+ O<sub>2</sub>Ti) showed pronounced colour variations with darkening or a tendency to grey-black and an increase in yellowing in the mixture. For zinc oxide (LC+OZn) the visual changes in colour were less intense, with darkening or greying and changes towards orangish colours and yellowing.

In the case of polymerized linseed samples (LP+ O<sub>2</sub>Ti) and (LP+OZn) the results for both pigments were very similar, darkening or tending towards grey-black as well as changes towards orangish colours from the increased chroma, and slight yellowing.

Finally, in the samples of linseed and Venetian turpentine with titanium oxide (LTV+ O<sub>2</sub>Ti) strong darkening or blackening was found together with increased chroma or tendencies towards orangish tones and yellowing. In the zinc oxide samples (LTV+OZn) the effect was practically identical to that of titanium oxide, but without notable yellowing.

The effect is unknown for this type of assay on the samples of polyvinyl Rhodorsil (PAV+ TiO<sub>2</sub>) and Mowilith (MWD) with the two white pigments (O<sub>2</sub>Ti and OZn) because the mixed material was lost from the support and thus could not be measured.

The effect at this stage of aging was the most evident in the results found. According to the sample in Table 7, with the exception of Mowilith Resin (MWR), the rest varied markedly in total colour, reaching maximum values of 17.89 in the case of the binder linseed with Venetian turpentine (LTV). Coinciding

with the above-mentioned cases, the increases continued to be far more significant in the natural samples than in the synthetic ones. With respect to the changes in luminosity, chroma, and hue, pronounced variations were found in the natural samples but no changes were found in the synthetic ones.

As opposed to the above cases, the samples containing zinc oxide showed major differences for the cases of natural binders both in total colour ( $\Delta E$ ) as well as chroma ( $\Delta L$ ), and hue ( $\Delta H$ ) while the synthetic ones remained without changes.

Sample	O <sub>2</sub> Ti								OZn							
	$\Delta E$	$\sigma$	$\Delta L$	$\sigma$	$\Delta C$	$\sigma$	$\Delta H$	$\sigma$	$\Delta E$	$\sigma$	$\Delta L$	$\sigma$	$\Delta C$	$\sigma$	$\Delta H$	$\sigma$
AD	<b>16.79</b>	0.37	<b>-8.84</b>	-0.04	<b>13.17</b>	0.07	<b>-5.48</b>	-0.16	<b>19.45</b>	0.49	<b>-11.98</b>	-0.28	<b>14.83</b>	0.43	<b>-3.83</b>	-0.08
ALM	<b>8.62</b>	0.25	<b>-3.46</b>	-0.07	<b>7.37</b>	0.15	<b>-2.84</b>	-0.08	<b>8.78</b>	0.21	<b>-1.8</b>	-0.02	<b>8.50</b>	0.17	<b>-1.27</b>	-0.03
D	<b>5.99</b>	0.10	<b>-1.51</b>	-0.02	<b>5.46</b>	0.02	<b>-1.94</b>	-0.04	<b>5.56</b>	0.15	<b>-1.56</b>	-0.02	<b>5.30</b>	0.01	<b>-0.65</b>	-0.01
LC	<b>12.25</b>	0.15	<b>-9.11</b>	-0.18	<b>2.57</b>	0.01	<b>-7.78</b>	-0.23	<b>6.95</b>	0.20	<b>-4.78</b>	-0.10	<b>3.78</b>	0.02	<b>-3.34</b>	-0.05
LP	<b>16.38</b>	0.25	<b>-8.8</b>	-0.04	<b>13.46</b>	0.05	<b>-3.1</b>	-0.06	<b>12.54</b>	0.21	<b>-6.08</b>	-0.12	<b>10.41</b>	0.25	<b>-3.44</b>	-0.05
LTV	<b>17.89</b>	0.28	<b>-13.24</b>	-0.38	<b>11.28</b>	0.22	<b>-4.17</b>	-0.01	<b>19.25</b>	0.27	<b>-14.15</b>	-0.28	<b>12.92</b>	0.14	<b>-1.85</b>	-0.01
EN	<b>3.05</b>	0.04	<b>-2.19</b>	-0.03	<b>1.83</b>	0.05	<b>-1.07</b>	-0.02	<b>1.2</b>	0.02	<b>-1.04</b>	-0.02	<b>-0.04</b>	0.00	<b>-0.6</b>	-0.01
ENR	<b>3.83</b>	0.09	<b>-2.09</b>	-0.01	<b>2.95</b>	0.06	<b>-1.26</b>	-0.03	<b>1.12</b>	0.02	<b>-0.66</b>	0.00	<b>0.86</b>	0.02	<b>-0.28</b>	-0.01
MWD																
MWR	1.95	0.04	-1.12	-0.02	1.16	0.02	-1.1	-0.02	1.06	0.01	-0.76	-0.01	0.65	0.00	-0.36	-0.01
PAV									2.92	0.04	-2.25	-0.04	1.77	0.03	-0.58	0.00

Table7. Mean values of differences in total colour ( $\Delta E$ ), chroma ( $\Delta L$ ), saturation ( $\Delta C$ ) and hue ( $\Delta H$ ) between pure pigments and each of the binders-media assayed under the D65 illuminant with infrared/heating and H<sub>2</sub>O aging.

Figure 5 shows graphically the differences in total colour ( $\Delta E$ ) for the different samples in the different aging treatments applied, natural aging, UV aging, and infrared-heating and H<sub>2</sub>O aging, the green line marking the limit of human visual perception.

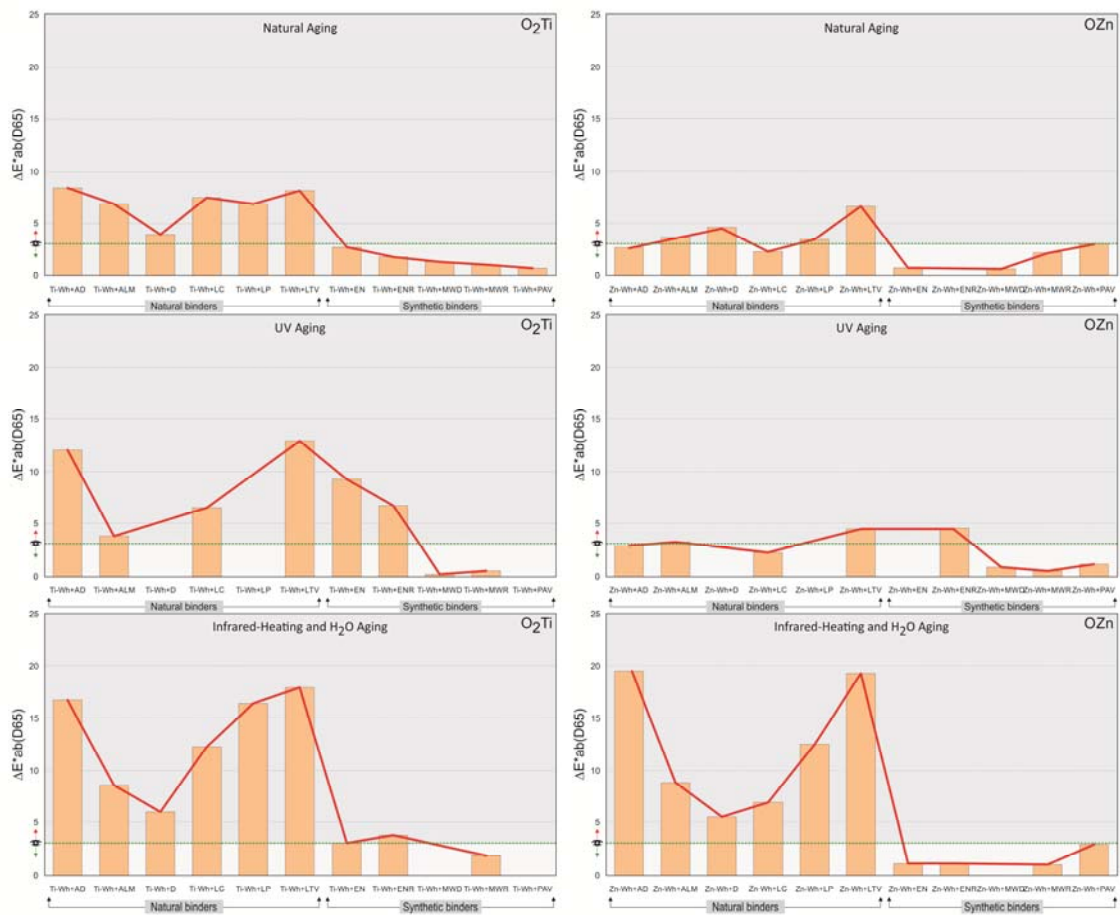


Figure 5. Graphic representation of the mean variations in total colour ( $\Delta E$ ) of the preparations (binder plus pigment) after the aging treatments. The broken green line indicates the limit of variability in total colour perceptible to the human eye.

Finally, illustrating the colour changes undergone by the different mixtures, the software used for colorimetric measurement provides simulations of the colour variations of the samples affected (Figure 6). A colour card was presented, showing the changes found in the different samples after the different assays (natural aging, UV-radiation aging, and infrared radiation plus atmospheric saturation with water). First, the pure pigment was exposed in each of the series to later include the colour simulation with different techniques, both for the titanium oxide pigment as well as for the zinc oxide pigment, appropriately labelled with abbreviations.

The symbol with an eye crossed out in green signifies that the samples had no changes recognizable by the human eye. Also, the symbol showing the eye crossed out in red means that the samples could not be measured due to deterioration undergone during the assays.





Figure 6. Simulated colour card using the software Spectra Magic de Konica Minolta. The first colour in each series corresponds to the pure pigment. It is followed by colour simulations with the different techniques.

Symbol of the eye crossed out in green = samples with variations unrecognizable to the human eye.

Symbol of the eye crossed out in red = samples not measured for deterioration.

#### 4. CONCLUSIONS

The use of mass spectrometry has enabled the rapid and reliable detection of the transformation of the organic compounds used as binders of the different samples prepared after the aging assays, indicating a consistent time course for these compounds.

The use of scanning electron microscopy revealed the textural changes in relation to the variations in luminosity and darkening of the samples, which in terms of visual colour translates as a trend towards grey or black.

The application of instrumental techniques in determining the colour proved key for the samples made, with respect to knowledge of the chromatic nature and performance of the elements present (pigments, binders), as well as with regard to the study of the conservation of patrimony and cultural heritage. The values of the colour differences (total colour,  $\Delta E$ ; luminosity,  $\Delta L$ ; hue,  $\Delta H$ ; and chroma,  $\Delta C$ ) among the different preparations of pigments and binders, before and after their exposure to the agents used, indicated which ones exerted the greatest effect, which could be quantified due to the instrumental nature of the control procedure followed.

In this study, the colour variations depended on the technique and on the pigment used, the impact varying according to the different parameters (luminosity, chroma, and hue). Luminosity (darkening) was the parameter most affected, with chroma in second place, and hue the least affected.

In general terms, the different techniques, to a greater or lesser degree reduced the luminosity of the pure pigment, while the effect on saturation (intensity of the whiteness) proved more diverse. With respect to hue or dominant wavelength ( $\Delta H$ ), the pigments were rather stable in the media assayed, the differences only in some cases appreciably exceeding values of 3 (detection-limit value of the human eye).

In the context of industry and the engineering of materials, the use of these mixtures globally generates major changes in the visual aspect of the objects, and therefore should be taken into account. In general, aging implies a loss of the physical conditions of the film, causing cracking and other damage, and therefore greater aging and loss of luminosity and shifts towards greys and blacks.

In relation to the impact of exposure to environmental agents, it was evident that the effect on the samples by infrared radiation and subsequent saturation was more pronounced than that of the other two assays (natural aging and UVA radiation).

Regarding physical durability and its material application, the samples with a binder of dammar (D) and both pigments ( $O_2Ti$  and  $OZn$ ), polymerized linseed (LP) also with both pigments ( $O_2Ti$  and  $OZn$ ), encaustic (EN+ $OZn$ ) and polyvinyl acetate (PAV+  $O_2Ti$ ) underwent complete deterioration under UV exposure and thus their industrial use is not advised. Similarly, the samples with a binder of vinyl emulsion MWD with both pigments ( $O_2Ti$  and  $OZn$ ), and acetate of polyvinyl (PAV+  $O_2Ti$ ) deteriorate under exposure to infrared radiation and environmental saturated humidity, and thus industrial use is not recommended, either.

Also, the alteration viewed at the microscopic scale was notable in the most aged samples and this implies marked changes in relation to the stability of properties that are required in these media to guarantee their desired performance.

With regard to the comparison to be made between the two pigments, and their relation to different media, the preparations with zinc oxide proved more stable than those made with titanium oxide, as reflected in the results of the colorimetric assay.

Overall, the techniques proved more affected with natural binders than with synthetic ones.

In terms of the alteration itself, the colour variation was towards orangish yellows with a special emphasis on the mixtures based on titanium oxide, the rest of the changes being fundamentally shifts towards grey-black.

A complete absence of colour variation is not possible when pigments are used with different techniques. With respect to the initial colour, any binder, adhesive, or ligand will chromatically alter the pigments, although it may be at levels not detectable by the human eye. Thus, for certain pigments the most optimal in terms of colour variation would be for those changes to be visually negligible or imperceptible.

Finally, it should be emphasized that these studies are useful as are the techniques applied to ascertain the action of a given pigment in combination with a certain binder to prevent possible variations in luminosity, chroma, or hue. This is fundamental both in the creative and artistic process as well as in conservation and restoration or in industrial manufacturing, where the characteristics of the original colour must be guaranteed to be chromatically stable over the maximum time period possible.

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