

Photodegradation kinetics of alkyd paints: the influence of varying amounts of inorganic pigments on the stability of the synthetic binder

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Abstract

Nowadays, understanding the degradation processes of artworks exposed to outdoor conditions is essential in order to conserve these objects. In fact, the continuous climate changes risk to increasingly affecting their chemical-physical stability, especially for modern and contemporary ones. For this purpose, in this study, the kinetics of photo-oxidation processes occurring in synthetic binders and their stability in mixtures with different inorganic pigments were investigated. The aim was not only to characterize the different degradation reactions over time but to study the photodegradation kinetics according to the different pigments and pigment/binder ratio (P/BM) chosen. A total of 9 paint samples were prepared by mixing the inorganic pigments (artificial ultramarine blue, hydrated chromium oxide green, and cadmium yellow) with alkyd resin, in three different pigment/binder (P/BM) ratios: 1:2, 1:3, and 1:6. The paint samples were exposed to artificial sunlight for up to 1008 h, documented by optical 3D microscopy and analysed by Infrared Spectroscopy (ATR-FTIR) and colourimetry every 168 hours. The results obtained demonstrate that the degradation processes of alkyd resin are influenced by the different inorganic pigment used and its amount/concentration in the mixtures. Evaluation of these different deterioration mechanisms took into account the morphological/colour changes, the chemical reactions, and the physical properties of the materials. This study should contribute to the field of conservation-restoration, such as finding protection strategies for surfaces from degradation agents.

Introduction

The production of polymers has increased rapidly in the last decades. Consequently, the study of contemporary art using such synthetic materials and the knowledge of proper preservation for these artworks has become very important on the international level [1]. With the development of synthetic organic chemistry at the beginning of the 20th century, a significant number of different organic materials have been used for creating artworks, especially alkyds. In addition to the chemical characterization of this polymer in the last 20 years, much attention has been given to the study of the chemical and physical factors, which influence the light stability of this binder, especially for the artworks exposed to solar radiation (outdoor environment) [2, 3]. Additionally, the presence of oxygen promotes photo-oxidation reactions, such as cross-linking, chain scission, and further oxidation reactions. Consequently, all these polymeric structural changes lead to the modification of mechanical properties, chemical stability, and degradation of this material [4]. Alkyds are oil-modified polyester resins composed of a polyhydric alcohol (generally glycerol), a polybasic carboxylic acid and siccative oils or free fatty acids. Due to the oil length, namely the weight percent of fatty acids in the structure of the alkyd resins, they are subject to curing and photo-degradation processes similar to drying oils [5]. The drying process occurs by autoxidation of unsaturated bonds of the fatty acid portion forming a cross-linked network. The consequence is that peroxy and hydroperoxy radicals may react with the alkyd chain leading to further cross-linking and/or β -scission reactions. The resulting degradation products are, for example, aldehydes, alcohols, and carboxylic acids with a lower molecular weight [6, 7]. Continuing the light ageing, other reactions contribute to the oxidation of alkyds. During auto-oxidation of the oil portion, chemical species such as

hydrocarbons, aldehydes, and ketones allow Norrish type I reactions (cleavage or homolysis into free radical intermediates) and chain-scission to take part in the oil degradation. In particular, Norrish type I is the main photo-degradation initiation reaction of aromatic polyesters, leading to the formation of free phthalic acid [6]. Furthermore, hydrogen abstraction (Norrish type II reaction) and products such as ketones, aldehydes, alkene, and carboxylic acids can be formed in the photochemical single state excitation. By the abstraction of hydrogen, alcohols, cyclic structures, carboxylic acids, and vinyl groups are produced. The main consequence of the alkyd resin photo-oxidation is the production of low molecular weight fractions, which are more easily evaporating or remain in the polymeric structure [6].

In the case of alkyd polymer, the long-term photo-oxidation reactions involved are different and have been studied in previous projects [8, 9]. In the evaluation of degradation processes occurring during artificial sunlight exposure, it is essential to consider also the contribution of pigments added to the paints, such as inorganic ones [5]. Different studies [10, 11] show that they can act as retardants or promoters of ageing reactions. Generally, pigments can be divided into two categories: photo-absorbers, which reduce the impact of light transmitted into the paint layer, and photo-promoters, which increase the photo-oxidation effect with the formation of free radicals. Moreover, characteristics of the pigments such as concentration, refractive index, and particle size have to be considered in these processes, as they can decrease or increase the penetration of radiation in the paint layer [12]. The importance of the research on the stability of artistic materials is fundamental not only because of the spoiled aesthetics of the artwork, but the risk of complete destruction. Mainly due to photodegradation, the outermost surface layer tends to fade and degrade more quickly, compromising the stability and durability of art objects over time.

Several studies using different analytical techniques were already carried out on alkyd binder, taking into account long-term UV exposure to mainly analyse the degradation reactions [13]. In the present work, the chemical surface changes on alkyd paints exposed to short-time artificial sunlight ageing were studied.

In fact, paint samples were exposed for 168, 336, 504, 672, 840, and 1008 hours (0–6 weeks) to artificial ageing, using spectral and intensity parameters comparable to outdoor solar radiation. Several paint samples were prepared by mixing each inorganic pigment (artificial ultramarine blue (PB29), hydrated chromium oxide green (PG18), and cadmium yellow (PY37)) with the synthetic binder. Three different pigment/binder (P/BM) ratios were chosen: 1:2, 1:3, and 1:6. The choice of different ratios allows understanding how the amount of pigment influences the degradation of the binders. Subsequently, the unaged and aged paint samples were analysed by Attenuated Total Reflection Infrared Spectroscopy (ATR-FTIR), colourimetric measurements, and morphological changes were evaluated by 3D Microscope. The main objective was to understand the degradation kinetics, which functional groups are more subjected to deterioration in the first 1008 h of light exposure and expand the knowledge on the different involvement of inorganic pigments in these oxidative reactions. Moreover, by ATR-FTIR analysis, it was possible to evaluate the influence of each pigment on the photo-oxidative reactions and in combination with the colourimetric measurements it was possible to elucidate the role of inorganic pigments at different concentrations (P/BM ratio) on the photodegradation process of binders and to clarify the degradation kinetics. In support of the results obtained, the measurements carried out by 3D microscope

allowed to observe the surface morphological changes and to compare the various degradation behaviours according to the different pigments used and their concentration in the mixture.

Experimental

Experimental

Sample preparation

Different samples were prepared by mixing pure Alkyd Medium 4 (Lukas®, Germany) with inorganic pigments (Kremer Pigmente, Germany), i.e. artificial ultramarine blue (PB29), hydrated chromium oxide green (PG18), and cadmium yellow (PY37). A detailed description of the paint samples is shown in Table 1. Different pigment/binder (P/BM) ratios were prepared depending on the consistency of the paint. They were cast on glass slides with a wet film thickness of 150 µm. In total 9 samples were prepared. The samples were dried at room conditions (ca. 22 °C and 50% relative humidity) for one week before starting the artificial ageing in the UV chamber. The samples were analysed every week (max. 1008 h exposure).

Table 1

List of materials analysed.

Binder	Chemical composition		Commercial name
Alkyd resin	Polymer oil-modified polyester-resin based on orthophthalic acid and pentaerythritol		Alkyd Medium 4 (Lukas®, Germany)
Pigment	Colour Index	P/BM ratio	Chemical composition
Artificial ultramarine blue	PB29	1:2, 1:3, 1:6	$\text{Na}_{6-10}\text{Al}_6\text{Si}_6\text{O}_{24}\cdot\text{S}_{2-4}$
Hydrated chromium oxide green	PG18	1:2, 1:3, 1:6	$\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$
Cadmium yellow	PY37	1:2, 1:3, 1:6	CdS

Artificial ageing

The light ageing which simulates natural sunlight was carried out in a UVACUBE SOL 2/400F UV chamber, produced by Dr. Hönle GmbH UV-Technology, Germany. The emitting radiation was supplied by a 910 W/m² Xenon Arc lamp with the possibility to provide radiations between 295 and ~ 3000 nm, similar to solar outdoor conditions. Temperature and relative humidity (RH) were separately measured in the chamber using the sensors AQL S500 (Aeroqual Limited, New Zealand). The chamber temperature during artificial ageing was around 38 °C, and the relative humidity varied between 10 and 20 % (RH). The radiation intensity was measured by using a UV-Meter Basic (Dr. Hönle, Germany). The Xenon lamp reached an approximate value of 170 W/m². According to the recent data provided by Central Europe, it is possible to assume that the radiation value obtained is similar to natural ageing caused by solar radiation [14, 15]. The artificial light exposure of acrylic and alkyd paints was carried out for 1008 h in

total. Taking into account that there are around 1000 h of sunshine per year (global approximation), it is possible to approximate the artificial sun ageing of 1008 h to around one year of natural outdoor sunlight exposure. To obtain the different times of ageing (168-1008 hours) on each paint sample, the glass slide was divided into 6 regions (Fig. 1). The regions which were not exposed to artificial light were contact-free covered with a silver-aluminium 100% reflective surface. The reflective cover was moved weekly to obtain the complete 1008 hours aged sample set.

3D Light Microscope

To monitor the different morphological changes due to artificial light ageing, the surface of each coloured layer was scanned by the Keyence VHX-6000 microscope (Keyence, Belgium). For each ageing week (from 0h to 1008 h) surface pictures were obtained. The objective chosen reaches a focus in the range of 100-1000 μm . The microscope is provided with a LED light source (5700 K).

For the 3D pictures, a magnification of 1000x was selected measuring a total area of 90925.77 μm^2 . To obtain the 3D depth profile of the surface, the total depth obtained is of 10 μm taking every 2 μm (pitch scans) a picture.

Colourimetric measurements

To obtain colourimetric values between unaged and aged samples, an SPM50 Gretag-Macbeth (XRite, Switzerland) was used. Measurements were carried out by a D65 light source with the 10° Standard Observer, 45°/0° geometry. The spot size measured is around 1 mm. The system was calibrated with an internal white reference. Three spots were measured per exposure and averaged using Microsoft Excel software (Microsoft®, USA). To determinate the colour changes between unaged and aged samples, CIELAB coordinates (L^* , a^* , b^*) and ΔE^* values were evaluated, according to the Commission Internationale de l'Éclairage 1976 (CIE 1976) [16].

Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR)

For the ATR-FTIR investigations, a LUMOS FTIR Microscope (Bruker Optics, Germany) in ATR mode with a germanium crystal was employed. The instrument is equipped with a photoconductive cooled MCT detector. Spectra were acquired in a spectral range between 4000 and 480 cm^{-1} performing 64 scans at a resolution of 4 cm^{-1} . Measurements were performed directly on the paint samples. The resulting spectra were collected and evaluated with the software OPUS® (Bruker Optics, Germany). Five measurement spots were chosen on each sample, acquired on unaged and aged paint samples. The spectra were averaged and baseline corrected. The chemical depth information obtained by the ATR-FTIR

measurements, considering the refractive index of the germanium crystal ($n_1 = 4.01$) and the angle of incidence of the IR beam ($\theta = 45^\circ$), in a spectral region between 4000 and 480 cm^{-1} , is around 0.65 μm .

Results And Discussion

Light Microscopy

Three-dimensional optical micrographs and topological images were recorded using a digital microscope VHX-6000 by a VH-Z100 objective with a zoom lens of 1000x. The 3D images of the paint surfaces (Figures 2, 3, and 4) show how the morphology of the paint layers changes during the light ageing process.

Observing the PB29 alkyd samples in Figure 2, the unaged areas of the samples show a glossier surface with the increase of the polymer component in the mixture (1:6). Moreover, the pores are more visible than in the sample with more pigment (1:2).

After a total of 1008 h of light ageing, different morphological changes are detectable, depending on the pigment/binder (P/BM) ratio. In the P/BM 1:6 mixture, the surface colour does not present evident changes; nevertheless, the pores number and their size increase. In the P/BM 1:2 mixture, the surface results dustier and opaque, the pigment grains are sharper, and the blue shade tends to discolour over time. This ageing effect is more noticeable when the pigment amount is high (1:2). In the colourimetric measurements chapter, the discussion about the colour changes is reported.

A similar behaviour is also observed for the PG18 alkyd samples (Fig. 3). In the 1:6 mixture, after 1008 h of ageing, the surface is less glossy and more porous. As for the blue sample, also in the green 1:2 mixture, the opacity increases over time probably due to the degradation of the binder and the pigment accumulation on the surface. However, contrary to the PB29 pigment, the PG18 tends to darken and this effect is especially visible in the mixture with a high amount of pigment (1:2). This morphological and colourimetric behaviour is also observable for the PY37 alkyd sample (Fig. 4).

ATR-FTIR results of alkyd paint degradation

ATR-FTIR spectra of alkyd binder (Alkyd Medium 4, Lukas) in mixtures with inorganic pigments (PB29, PG18, PY37) at different P/BM ratios (1:2, 1:3, and 1:6) were collected after 0, 168, 336, 504, 672, 840, and 1008 h of artificial sunlight ageing.

For the determination of the light degradation effects of alkyd binder mixed with inorganic pigments (PB29, PG18, and PY37), the ATR-FTIR absorption bands of the alkyd binder are labelled according to Table 2 [17, 18]. Using the ATR-FTIR spectrum of unaged alkyd paint (P/BM 1:2), mixed with PB29, it is possible to characterise the main absorption bands, as shown in Figure 5.1. The unaged spectra of the other mixtures (P/BM 1:3 and 1:6) are not depicted as they show the same absorbance bands but with

different intensities depending on the binder content. In this case, a significant contribution from the oil and phthalic component is identified. The main absorption bands that identify these two components are at 1724 cm^{-1} related to the C=O stretching vibration, and at 2926 , 2854 , 1465 , 1451 , and 1388 cm^{-1} related to the CH_2 and CH_3 stretching and bending (asymmetric and symmetric).

However, the phthalic groups can be identified mainly by absorption bands at 1600 and 1588 cm^{-1} corresponding to C=C stretching aromatic ring, at 1260 and 1114 cm^{-1} related to C-O-C symmetric stretching, and at 741 and 709 cm^{-1} due to the aromatic out-of-plane bending [19, 20]. By comparing the unaged and 1008 h light aged results, significant chemical changes on the surface are detected.

The results are evaluated according to the type of pigment used, the P/BM ratios and also the contribution of the inorganic components to the degradation process. In the case of alkyd binder with PB29 (Figure 5.1), after 1008 h of ageing the intensity of the broad OH stretching band at 3244 cm^{-1} is quite increased, above all in the sample with high amount of binder (Figure 5.1d), whereas the $(\text{C-H})\text{CH}_2$ asymmetric and symmetric stretching at 2926 and 2854 cm^{-1} decreased. It is due to the hydrogen abstraction and the oxidation of the double bonds, respectively [21]. The same decreasing trend is observed for the carbonyl band at 1724 cm^{-1} . Only in the paint with a high amount of binder, this band can still be detected after 1008 h of exposure. Furthermore, the shape of the band gets broader due to the ageing of the oil component in the alkyd binder, which is caused by hydroperoxides and peroxides reactions during photochemical degradation, forming oxidation products such as aldehydes, ketones, and carboxylic acids (at 1735 , 1720 , and 1710 cm^{-1}) [22].

Considering the spectral changes of the inorganic pigment PB29 in the mixture, the band at 1068 and 984 cm^{-1} , related to the Al,Si-O_4 asymmetric stretching, increases depending on the ageing time and its amount in the paint mixture [23]. As shown in Figure 5.1b, additional pigment bands at 691 and 656 cm^{-1} absorption vibrations, related to the Al,Si-O_4 symmetric stretching, are registered. Moreover, after the maximum exposure time performed, the small band at 470 cm^{-1} is increased. It is identified as the O-Si-O bending vibration [24]. The apparent increase of the spectral signal of PB29 characteristic absorption bands indicates that the oxidation of the alkyd binder functional groups causes an accumulation of the pigment particles on the surface of the paint layer [25, 26]. This chemical-physical phenomenon is so prominent in the alkyd paints because of the oil component. The latter is very reactive to the oxidative elements present in the surrounding environment (such as oxygen, sunlight, and O_3) leading to Norrish photo-cleavage reactions and the formation of free-radicals able to make the polymeric film unstable [27].

In Figure 5.2, the ATR-FTIR spectra of alkyd binder in mixture with PG18 in different P/BM ratio (1:2, 1:3, and 1:6) aged for 1008 hours are presented in comparison to the unaged P/BM 1:2 mixture. In general, all the main absorption bands of the alkyd binder are present (Table 1) but, after the light ageing, the spectra show a decreasing trend of the binder absorption bands. The worst degradation is observed for the mixtures with a high amount of pigment (Figure 5.2b). Similar to the PB29 results, the intensity of the PG18 bands at 552 and 493 cm^{-1} (of the oxide part) increase over time, due to the degradation and partial

evaporation of the binder compounds. Comparing the spectrum of the unaged sample with the aged ones, the OH stretching band at 3066 cm^{-1} increased with an increasing amount of pigment in the paint (Figure 5.2b), contrary to the results obtained for PB29 mixtures. It is due to the fact that this absorption band is mainly assigned to the hydrated component of the pigment which, as previously described, increase after ageing. Another absorbance band which is assigned to the pigment at 1283 cm^{-1} is registered during the light-ageing process. In combination with the band at 1252 cm^{-1} , which is still present after ageing, it can be related to the low content of chromium borate necessary for the production of the hydrated chromium oxide green pigment [28, 29].

In the case of alkyd paints mixed with PY37, the ATR-FTIR spectra are quite different from the results obtained for PB29 and PG18. Furthermore, the OH stretching band in this case at 3230 cm^{-1} increases with ageing time, especially in the paint sample with a higher amount of binder (Figure 5.3d). However, by comparing the spectrum of the alkyd sample in Figure 5.3d (P/BM ratio 1:6) with the paint sample mixed with the PB29 (Figure 5.1d), it is possible to observe that the carbonyl group C=O at 1724 cm^{-1} decreases more in the blue paint sample, whereas in the yellow paint it tends to be broader.

Table 2

ATR-FTIR absorption band assignment of binders and pigments employed acrylic.

Alkyd Wavenumber (cm^{-1})	Assignment	
2926 - 2854	(C-H)CH ₂ asymmetric - symmetric stretching	
1724	C=O stretching (oil and phthalate)	
1600 - 1588	C=C stretching aromatic ring (phthalate)	
1465 - 1451	CH ₂ and CH ₃ asymmetric bending	
1388	CH ₃ symmetric bending	
1260 - 1114	C-O-C symmetric stretching (phthalate)	
741 - 709	Aromatic out-of-plane bending (phthalate)	
Inorganic pigment	Wavenumber (cm^{-1})	Assignment
Artificial ultramarine blue (PB29)	1068 - 984	Al,Si-O ₄ asymmetric stretching
	691 - 656	Al,Si-O ₄ symmetric stretching
Hydrated chromium oxide green (PG18)	3066	O-H stretching
	552 - 493	Cr-O vibrations
Cadmium yellow (PY37)	< 450	Below detector cut-off

Photodegradation kinetics

The time-dependent behaviour of the alkyd binder in the paint samples was evaluated by the integration of the carbonyl group C=O band (1724 cm^{-1}) over time (Fig. 6). This specific band was chosen for the integration as it shows strong intensities, is not overlapping with other bands and is the most representative band for the binder. In Figure 6, the degradation behaviour of the different pigments with alkyd binder mixed in ratios 1:2, 1:3, and 1:6 are presented. Generally, the degradation of the binder,

shown by a decrease of the C=O area values, is already observed after 168 h of ageing for all three pigment mixtures at P/BM ratios 1:2, whereas for those with P/BM ratios 1:6, it can be observed approximately after 336 h. The kinetic trend changes depending on the type of pigment used.

In mixtures with PB29, the degradation of the organic binder is higher than for PG18 and much higher than for PY37. The contribution of the pigments is important as they enhance (with PB29) or decrease (with PY37) the effect of light irradiation on the degradation process of the binder. Comparing the blue and the yellow mixtures with P/BM 1:2, the decrease of the binder at 1724 cm^{-1} is much faster in the blue paint. On the other hand, increasing the binder amount (P/BM 1:6) in all paint mixtures, the degradation of the organic component is reduced.

For a more detailed evaluation of the binder degradation rate, according to the pigment and the P/BM ratio used, the different numerical values obtained by the integration of the C=O carbonyl band in the paint mixtures were compared (Table 3). The area values (considering the integration of the carbonyl group C=O around 1724 cm^{-1}) of each sample for every week (168 h) of ageing were evaluated [30].

The values obtained were subsequently evaluated according to the difference between the area value of the unaged sample and after 1008 h of exposure $\Delta(\text{C=O}_{\text{unaged/aged}})$.

The evaluation showed (Fig. 6) that there is a direct correlation between light exposure time and degradation. In fact, with high values of $\Delta(\text{C=O}_{\text{unaged/aged}})$, the process of photo-oxidation on the surface is more damaging, with the consequent decrease of the C=O band over time. In particular, according to the values $\Delta(\text{C=O}_{\text{unaged/aged}})$, it is possible to notice that in the samples with a high amount of binder (P/BM 1:6) the photo-oxidative process is reduced, while in the samples with an high amount of pigment (P/BM 1:2), the values $\Delta(\text{C=O}_{\text{unaged/aged}})$ increase, suggesting a more oxidative effect. However, this trend changes according to the pigments used. Comparing the three different coloured paints, this difference is more significant in PB29 paints than in PY37. Moreover, with the increase of the amount of binder, these values $\Delta(\text{C=O}_{\text{unaged/aged}})$ remain quite stable for PB29 and PG18, while for PY37 they decrease more quickly. This numerical difference indicates that with the same amount of pigment, the PB29 facilitates the interaction of light irradiation with the surface of the paint through a more rapid decomposition of the alkyd binder.

Table 3

Integrated ATR-FTIR band areas of C=O stretching band at 1724 cm^{-1} of alkyd resin in unaged and 1008 h aged samples. The Δ area values indicate the difference between the C=O values of unaged and 1008 h aged paint samples.

Sample	Ageing (time)	Area value C=O	$\Delta(C=O_{\text{unaged/aged}})$
PB29 + Alkyd Medium 4 (1:2)	Unaged	18.7	17.2
	1008 h	1.54	
PB29 + Alkyd Medium 4 (1:3)	Unaged	16.8	16.5
	1008 h	0.25	
PB29 + Alkyd Medium 4 (1:6)	Unaged	10.5	10.4
	1008 h	0.14	
PG18 + Alkyd Medium 4 (1:2)	Unaged	24.2	12.5
	1008 h	11.7	
PG18 + Alkyd Medium 4 (1:3)	Unaged	18.8	10.8
	1008 h	8.02	
PG18 + Alkyd Medium 4 (1:6)	Unaged	16.9	9.2
	1008 h	7.7	
PY37 + Alkyd Medium 4 (1:2)	Unaged	21.7	7.7
	1008 h	14.0	
PY37 + Alkyd Medium 4 (1:3)	Unaged	22.1	6.4
	1008 h	15.7	
PY37 + Alkyd Medium 4 (1:6)	Unaged	22.6	1.4
	1008 h	21.2	

Colourimetric measurements

In Table 4, the colourimetric results of unaged and 1008 h UV-aged alkyd paint samples are shown. The results include the colourimetric changes in the values of the lightness/darkness (L^*), red/green (a^*), yellow/blue (b^*), and the total colour change from 0 h to 1008 h exposure (ΔE^*). The ΔE^* values obtained from each coloured paint and P/BM ratio were kinetically evaluated and compared. Observing Figure 7, the greatest change of colour is recorded for PB29 paint in P/BM ratio 1:2 that tends to decrease with the increase of binder amount. A similar trend is detected for PG18 and PY37 paints but less significant than for the blue paint. Generally, a quite significant difference in the shift of the L^* , a^* , and b^* coordinates between the unaged and aged paint samples is observed in the alkyd paints, which confirm the instability of this binder when exposed to the artificial light (Table 4).

Comparing all the colourimetric values of the three inorganic pigments, the PB29 alkyd paint samples have the most significant shift of a^* and b^* between unaged and aged samples, showing a strong reduction in red and blue, respectively. The decreasing of a^* and b^* values, and the overall increase of the L^* parameter might be due to changes in the surface roughness of the paints [31]. In fact, after ageing the macroscopic properties of the film change, becoming stiffer and more brittle, probably due to cross-linking of the residual olefinic unsaturation [32].

Another deterioration factor is the colour shift, which tends to lighten (PB29) or darken (PG18 and PY37) over time. This behaviour was studied by evaluating the L^* values according to the different pigment and P/BM ratio used. During the light exposure, the L^* values for alkyd paints mixed with PB29 and PY37

increase whereas with PG18 they decrease. As reported in the literature [33, 34], artificial ultramarine blue (PB29) has a significant loss of its blue colour when mixed with alkyd resin after light irradiation.

This effect is probably due to the chromophoric S-anions release after the opening of the sodalite cages of pigment, leading to the discolouration of the pigment itself. Cadmium yellow (PY37) and hydrated chromium oxide green (PG18) are generally considered lightfast pigments, so their different brightness changes (L^*) are not completely clear [35]. During ageing, some chemical properties of the paints are lost as the paint film is gradually attacked by oxidising agents, leading to the breakdown of the polymer molecules into smaller fragments. This phenomenon increases if the pigment concentration is high, as during light exposure the pigment particles placed on the surface will be more subject to the action of photodegradation leading to the fading or darkening of the colour [36]. In some cases, the loss of the chemical-mechanical properties of the binders mixed with some pigments (as for PB29) leads to the highest fragility of the paint on the surface, becoming almost powdery (chalking).

The colour and morphological changes can be also explained by taking into account specific chemical-physical factors, characteristic for each pigment, namely the refractive index and the particle size. Depending on the refractive index (R.I.) of the different materials and their different particle size (P.S.), it is possible to evaluate the effect of the light irradiation to the paint surface enhancing or limiting the degradation of the polymeric medium. If a paint film contains a pigment with a high refractive index, the light tends to be more bent or refracted at the surface [37]. Observing the R.I. values of the analysed pigments [38-42], PY37 has a higher R.I. (approx. between 2.35-2.48) than the other two inorganic pigments (PB29 1.5, PG18 1.62-2.12). Therefore, the light radiation will have a higher impact on the blue paints followed by the green paint sample. These results are in accordance with the ATR-FTIR measurements, indicating a more aggressive degradation of the polymeric binder. Moreover, the light scattering imparted by diffraction is further affected by the particle size. In fact, the smaller the particle size and the higher R.I. are, the more the light beam has a tendency to be scattered [43, 44]. In particular, the granulometric values of the inorganic pigments (reported from Kremer Pigmente) reveal that the particle size is smaller in PY37 (0.5 μm) and higher in PB29 and PG18 (both 2.50 μm), confirming the previous considerations [45, 46]. However, being a mixture, it is also necessary to consider the influence of the refractive index of the binding medium, the dispersion level of the pigment (i.e. the degree of aggregation of the particles), the proportion of pigment in the vehicle, called pigment volume concentration (PVC), and the thickness of the paint layer [47].

Furthermore, the refractive index is not a constant value, but changes over time, also influenced by the P/BM ratio in the mixture and the type of pigment employed. Therefore, from the physical point of view, the different morphological and colourimetric changes should be investigated in more detail, taking into account the various components present in the paints and their importance in the degradation process.

In the examined case of study, the significant degradation of the alkyd binder is not entirely associated with the R.I. aspect, but predominantly the autoxidation of unsaturated bonds of the fatty acid portion contributes to the photo-degradation of the whole paint layer [5, 6].

Table 4

L* a* b* values related to unaged, and 1008h aged alkyd paints. Total colour change, calculated as the difference of unaged and aged samples after 1008 h (ΔE^*), is indicated.

Mixtures		Unaged	1008 h	ΔE^*
Alkyd+ PB29 (P/BM 1:2)	L*	28.43	28.66	23.8
	a*	29.23	15	
	b*	-60.66	-41.55	
Alkyd + PB29 (P/BM 1:3)	L*	26.62	29.5	18.5
	a*	10.30	9.23	
	b*	-22.87	-40.49	
Alkyd + PB29 (P/BM 1:6)	L*	27.58	25.86	5.48
	a*	15.55	10.42	
	b*	-32.73	-33.6	
Alkyd + PG18 (P/BM 1:2)	L*	28.35	24.01	9.81
	a*	-11.09	-19.6	
	b*	-0.62	-2.60	
Alkyd + PG18 (P/BM 1:3)	L*	30.80	25.27	8.02
	a*	-11.09	-16.75	
	b*	-0.60	-1.93	
Alkyd + PG18 (P/BM 1:6)	L*	22.74	28.15	7.98
	a*	-21.58	-15.85	
	b*	0.32	-0.94	
Alkyd + PY37 (P/BM 1:2)	L*	76.04	76.95	19.8
	a*	28.79	28.14	
	b*	87.93	84.34	
Alkyd + PY37 (P/BM 1:3)	L*	75.95	77.01	11.01
	a*	27.90	25.39	
	b*	95.11	84.45	
Alkyd + PY37 (P/BM 1:6)	L*	73.16	75.75	3.76
	a*	22.16	22.23	
	b*	101.47	81.65	

Conclusion

The chemical surface changes on alkyd paints, mixed with inorganic pigments and exposed to short-time artificial sunlight, were documented by optical 3D Microscope and studied by ATR-FTIR and colourimetric analysis. To monitor the different degradation behaviour of each paint sample, three different pigment/binder (P/BM) ratios were chosen: 1:2, 1:3, and 1:6. The paint samples were exposed in total for 1008 h to artificial sunlight, using similar characteristics to outdoor solar conditions. The main degradation reactions that occur in alkyd paints during light ageing are:

- Degradation of the alkyd binder already after 168h, shown by an intensity decrease of the functional groups of the alkyd resin over time. This trend is most evident in the mixtures with the blue pigment PB29, followed by PG18, whereas in those with the yellow pigment PY37, it is more stable.

- In all paint samples, the pigment bands (at 984 cm^{-1} for PB29 and $552\text{-}493\text{ cm}^{-1}$ for PG18) show an increase during light exposure. This phenomenon is due to the decomposition of the binder, where its main functional groups tend to oxidise, leading to an accumulation of pigment particles on the paint surface.
- The kinetic evaluation of ΔE^* shows that the PB29 alkyd mixture (P/BM 1:2) presents the highest colour change, followed by PY37 and PG18.
- Morphological changes are visible by observing the 3D images of the paint surfaces. (Figures 2, 3, and 4) it is possible to notice how the mixtures during ageing present morphologies more rigid, opaque and with a dusty appearance. The surfaces become less bright and stiffer for paints with P/BM 1:2 over time exposure. Generally, when the content of the pigment is low, the light degradation behaviour is reduced.

These phenomena can partially be explained by taking into account two specific chemical-physical factors, the refractive index (R.I.) and the particle size (P.S.). PY37 has a higher R.I. than PB29 and PG18. For this reason, the light irradiation can penetrate more in-depth in the layer, leading to a more degrading effect of the polymeric binder [46]. The particle size is lower for PY37 than in PB29 and PG18; so smaller the particle size of the pigment is, the more the light has a tendency to be scattered.

In conclusion, the paint samples exposed to artificial light ageing show degradation processes that vary according to the binder, the inorganic pigment, and the P/BM ratio employed. The choice of pigment can cause the increase of several photo-oxidative effects on the binder; in fact, PB29 causes more degradation effect on the surfaces than the PY37 and PG18. Additionally, a high amount of pigment in the paints leads to a high degradation of the binder.

List Of Abbreviations

P/BM: Pigment / Binding Medium; ATR-FTIR: Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy; UV: Ultraviolet; PB28: Pigment Blue 28; PG18: Pigment Green 18; PY37: Pigment Yellow 37; RH: Relative Humidity; CIE: Commission Internationale de l'Éclairage; R.I.: Refractive Index; P.S.: Particle Size; PVC: Pigment Volume Concentration.

Declarations

Availability of data and materials

Additional data about kinetics, colourimetry, and 3D images are available upon request.

Competing interests

The authors declare that they have no competing interests.

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Authors' contributions

LP developing the research question, preparation of paint samples, acquisition, evaluation and interpretation of data, writing the article. RW supervising the acquisition and interpretation of data, contributing to the writing and the revision of this article. MS supervising the research work and revision of the article. All authors read and approved the final manuscript.

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Figures

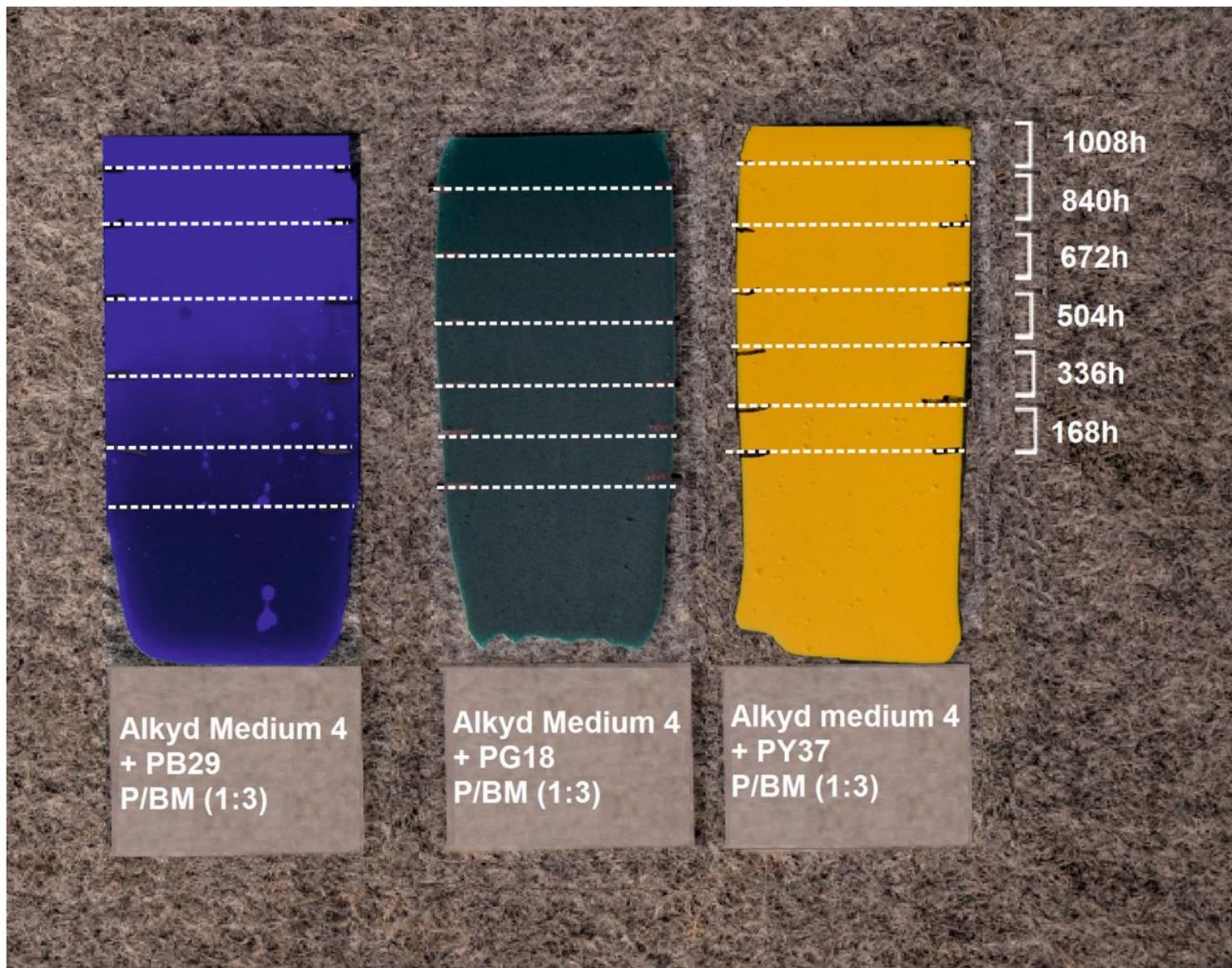


Figure 1

Representation of three paint samples with P/BM ratio 1:3; from left Alkyd Medium 4 + PB29, Alkyd Medium 4 + PG18, Alkyd Medium 4 + PY37. They were exposed to 168, 336, 504, 672, 840, and 1008 h of artificial sunlight ageing.

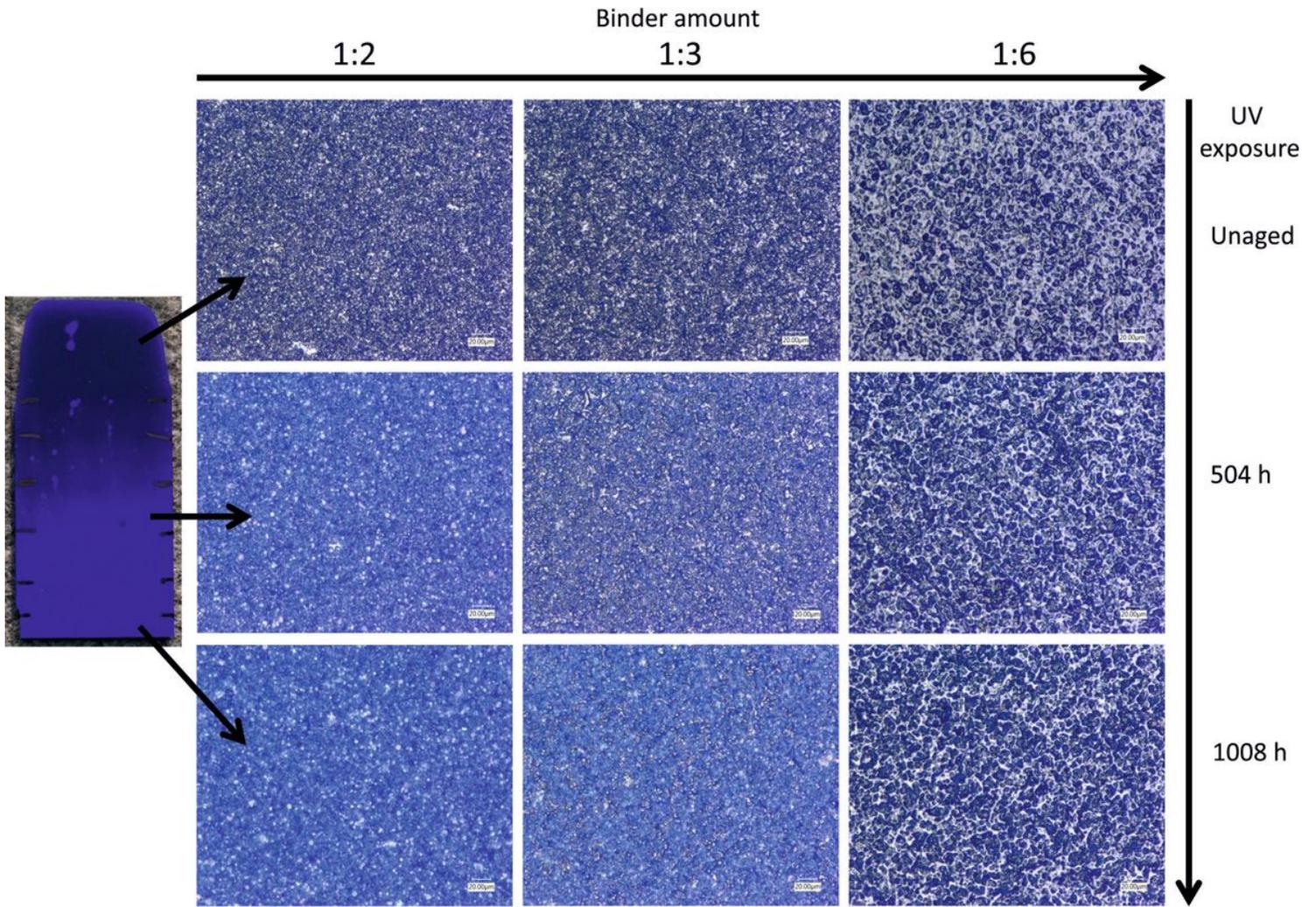


Figure 2

Morphological overview by 3D image (1000x) of PB29 alkyd samples. From left to right the samples are displayed according to the different P/BM ratio, whereas from upper to lower depicts the unaged, 504 h, and 1008 h ageing. On the left the mock-up (P/BM 1:2) is shown.

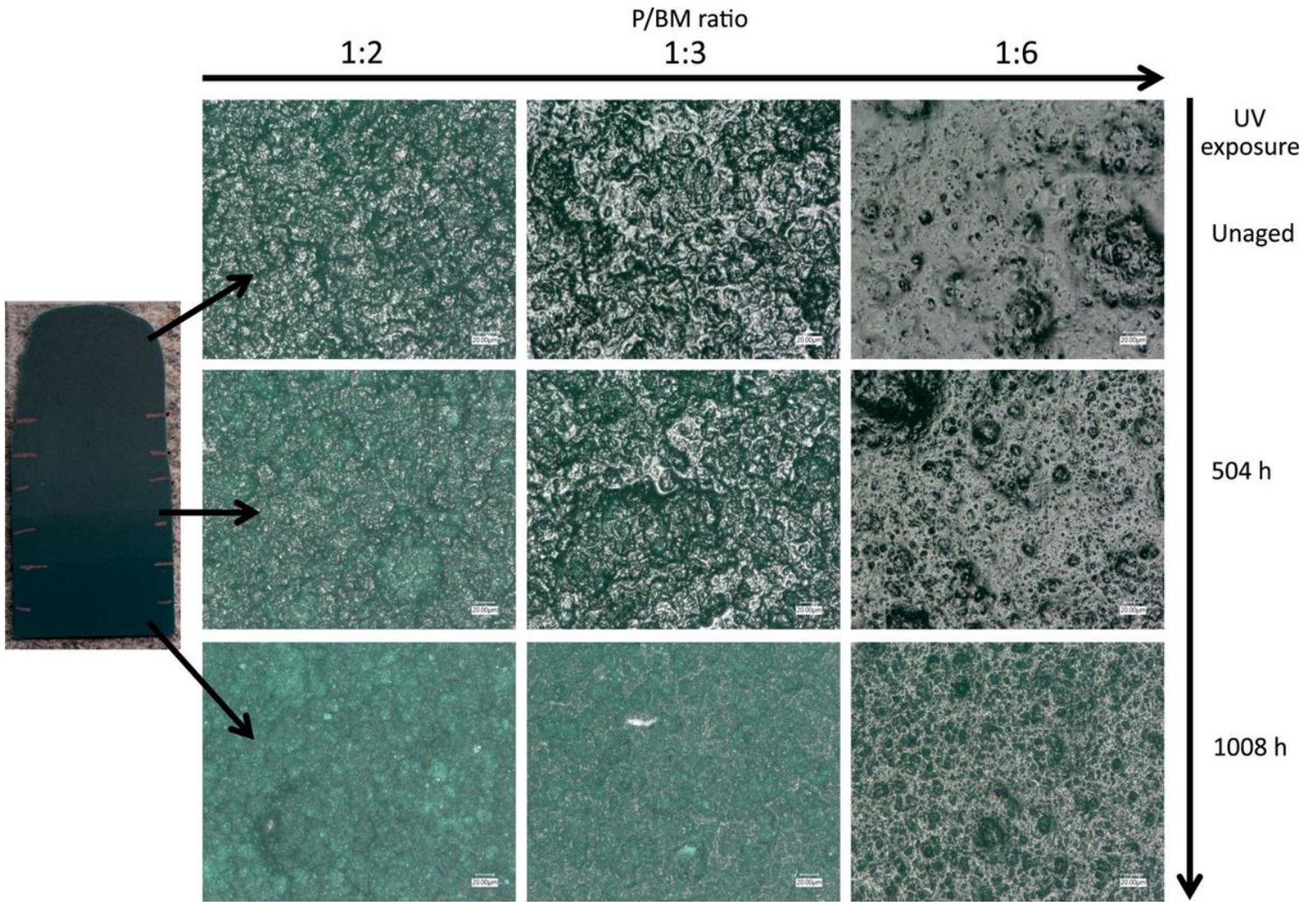


Figure 3

Morphological overview by 3D image (1000x) of PG18 alkyd samples. From left to right the samples are displayed according to the different P/BM ratio, whereas from upper to lower depicts the unaged, 504 h, and 1008 h ageing. On the left the mock-up (P/BM 1:2) is shown.

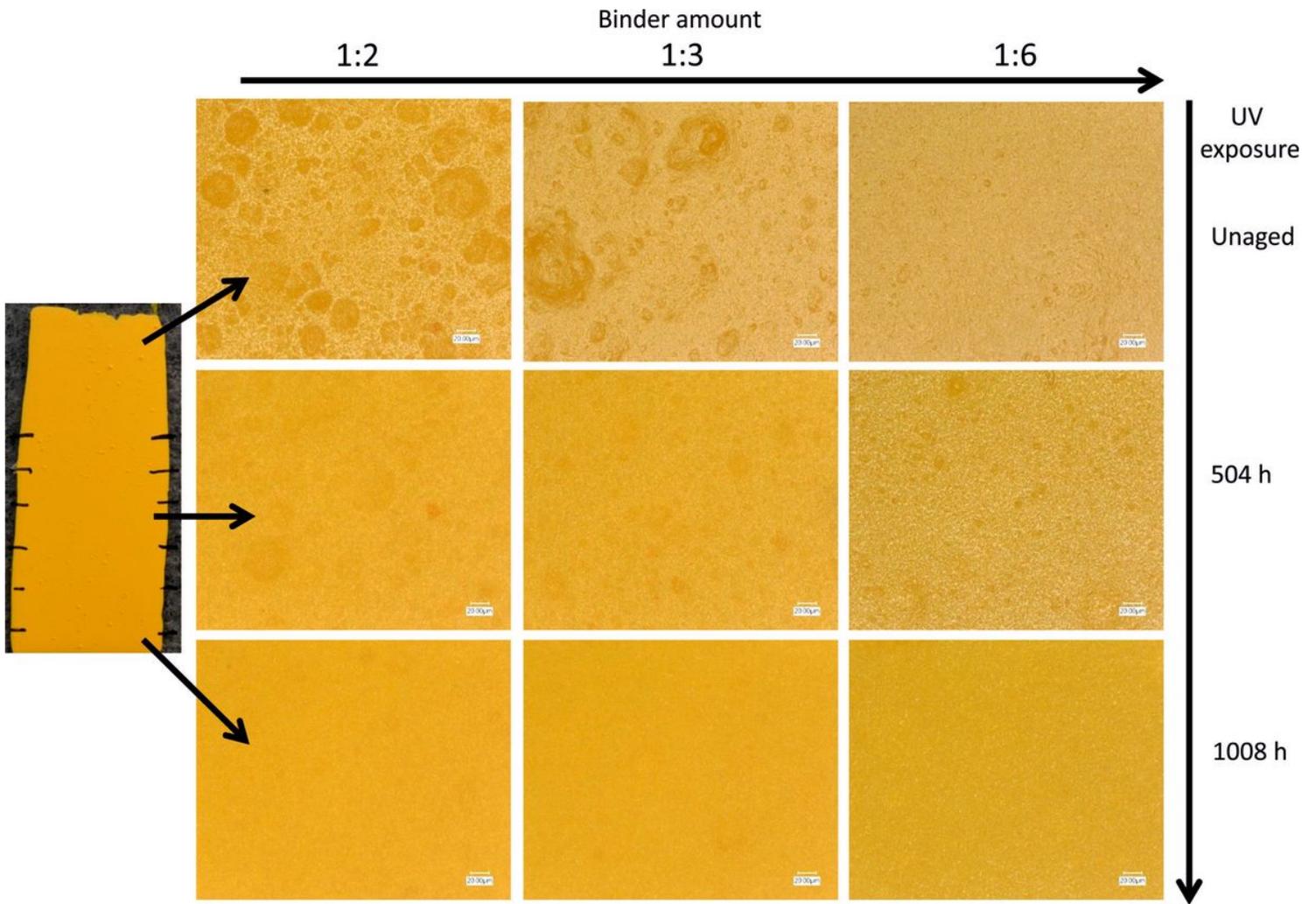


Figure 4

Morphological overview by 3D image (1000x) of PY37 alkyd samples. From left to right the samples are displayed according to the different P/BM ratio, whereas from upper to lower depicts the unaged, 504 h, and 1008 h ageing. On the left the mock-up (P/BM 1:2) is shown.

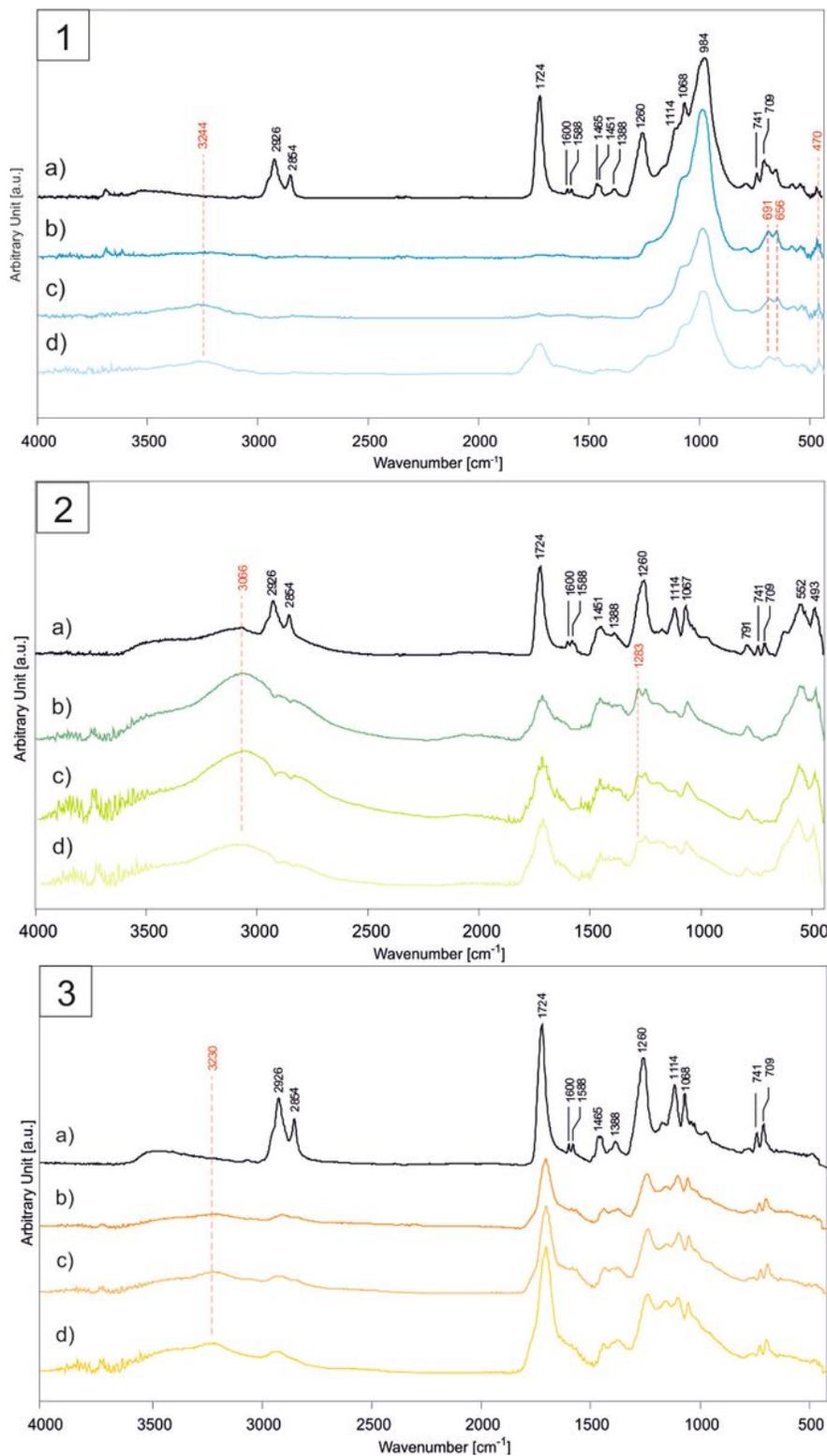


Figure 5

ATR-FTIR spectra of alkyd binder in mixture with inorganic pigments: 1) PB29, 2) PG18, and 3) PY37. For each coloured mixture graph, a) unaged sample P/BM 1:2, and after 1008 h of UV exposure: b) P/BM ratio 1:2, c) P/BM 1:3, and d) P/BM 1:6 are compared.

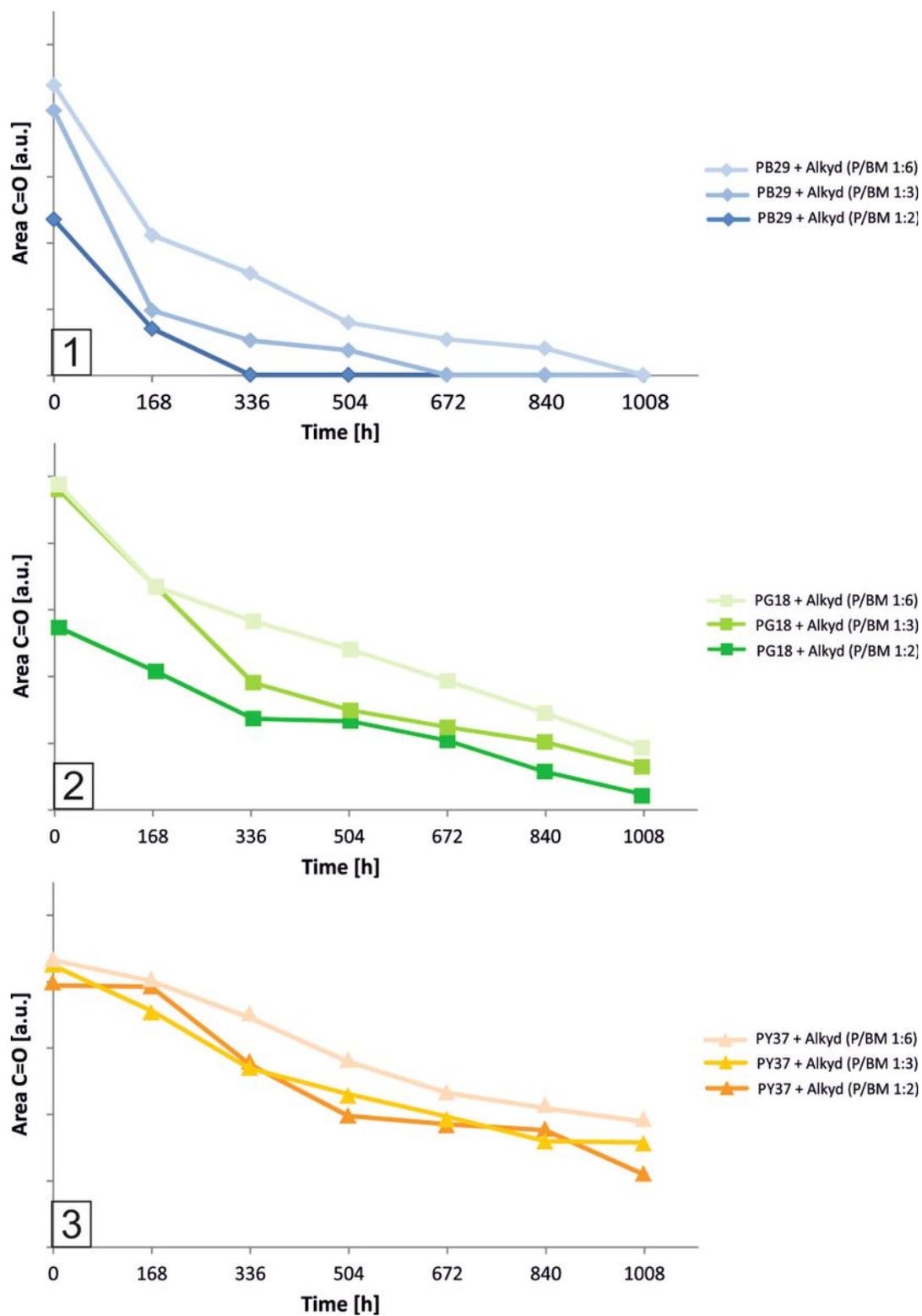


Figure 6

Photodegradation kinetics observed from ATR-FTIR spectra of alkyd paints with 1) PB29, 2) PG18, and 3) PY37, in different ratio.

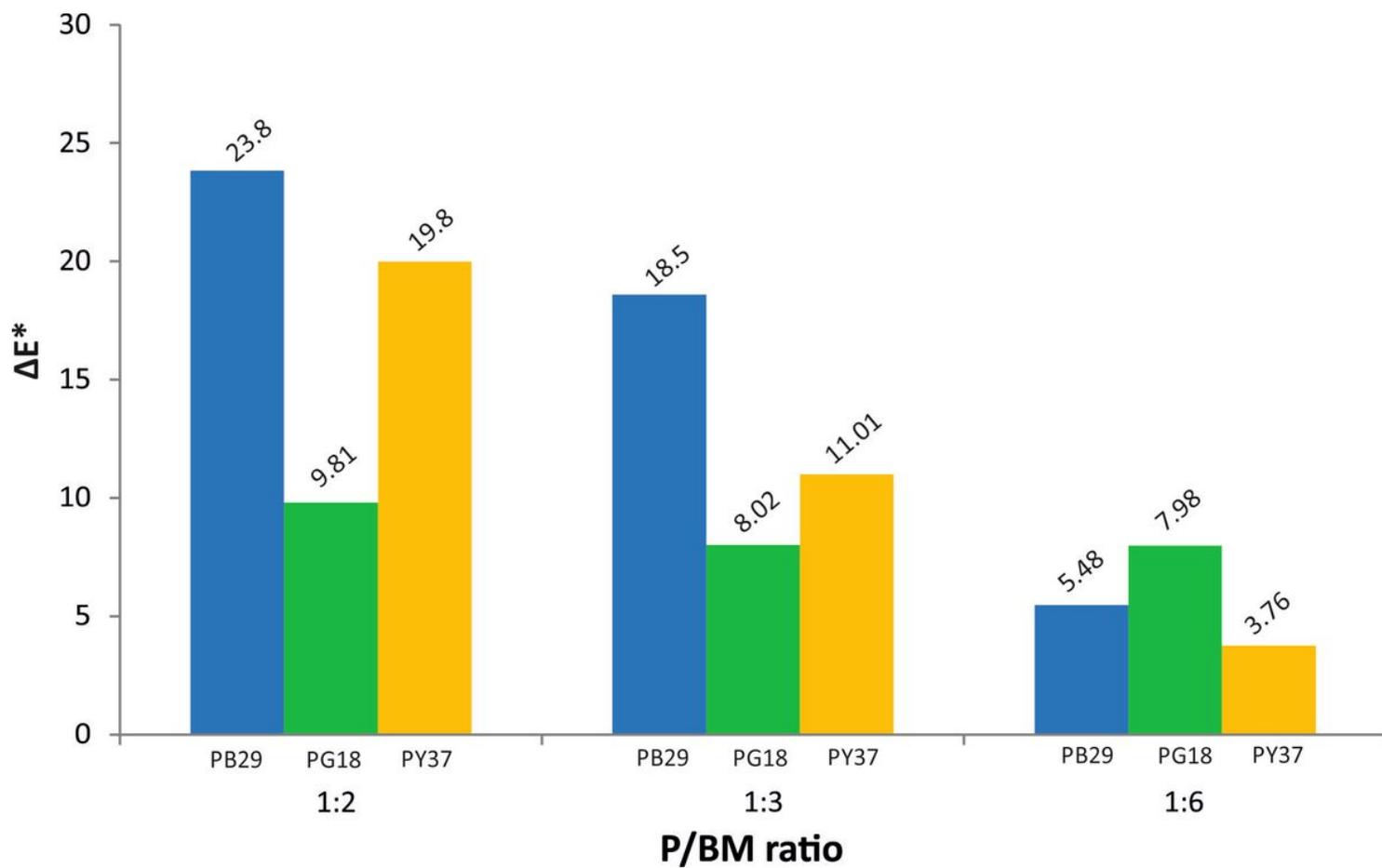


Figure 7

Photodegradation kinetics observed from ΔE^* changes of alkyd paints over UV exposure.