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Photodegradation behaviour of synthetic paint binders: comparative study of selected acrylic, alkyd, PVAc and nitrocellulose products

Fotodegradação de ligantes de tintas sintéticas: estudo comparativo de produtos selecionados de acrílico, alquídico, PVAc e nitrocelulose

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Abstract

Modern and contemporary artworks often present complex conservation challenges due to the widespread use of synthetic paints and the diversity of their formulations. This study investigates changes induced by photodegradation in selected commercial products representing four major classes of synthetic binders – acrylic, alkyd, polyvinyl acetate, and nitrocellulose – commonly used in twentieth-century painting. Samples of artistic paints, polymer dispersions, alkyd enamels, and nitrocellulose varnish were artificially aged under UV radiation and examined by ATR-FTIR spectroscopy, colourimetry, and digital microscopy. The results revealed distinct degradation patterns within and between binder classes, including variable colour shifts and characteristic spectral changes linked to oxidation and polymer chain scission. The findings emphasise the influence of diverse paint formulation factors, seen as a whole system, on material stability and the need for reference spectra of aged materials to support identification in conservation studies. The research forms part of a broader project on synthetic paint binders in post-war Polish art.

KEYWORDS
Contemporary art
Modern paints
Synthetic binding media
Light ageing
FTIR
Colourimetry

Resumo

As obras de arte modernas e contemporâneas apresentam frequentemente desafios de conservação complexos, devido à utilização generalizada de tintas sintéticas e à diversidade das suas formulações. Este estudo investiga as alterações induzidas pela fotodegradação em produtos comerciais selecionados que representam quatro classes principais de ligantes sintético: acrílico, alquídico, acetato de polivinilo e nitrocelulose, comumente utilizados na pintura do século XX. Amostras de tintas artísticas, dispersões de polímeros, esmaltes alquídicos e vernizes de nitrocelulose foram envelhecidas artificialmente sob radiação UV e examinadas por espectroscopia ATR-FTIR, colorimetria e microscopia digital. Os resultados revelaram padrões de degradação distintos dentro e entre as classes de ligantes, incluindo mudanças de cor e alterações espectrais características ligadas à oxidação e à cisão da cadeia polimérica. As descobertas enfatizam a influência de diversos fatores de formulação da tinta, na estabilidade do material e a necessidade de espectros de referência de materiais envelhecidos para apoiar a identificação em estudos de conservação.

PALAVRAS-CHAVE
Arte contemporânea
Tintas modernas
Ligantes sintéticos
Envelhecimento com luz
FTIR
Colorimetria

Introduction

Synthetic resins have been used as binding media in paints since the late 1920s. While the introduction of acrylic emulsion paints in the early 1960s marked a turning point in artists' adoption of synthetic paints, many had already employed products originally intended for household or industrial applications, which also contained synthetic binders [1]. The diversity of paint types used by twentieth-century artists poses a considerable challenge for conservators, as their response to conservation treatments and environmental conditions varies greatly.

The history of the use of modern paints, described by Western researchers in the context of artistic and industrial products, does not necessarily reflect the situation in the countries of the former Eastern Bloc in this part of Europe. Between 1944 and 1989, Poland remained under the Soviet Union's influence. The consequences of the war and the “Iron Curtain” delayed both the production and availability of synthetic paints compared to Western Europe and the United States [2]. At the same time, the chronic shortages of professional art supplies pushed many Polish artists to use substitute products and to experiment with non-traditional techniques [3].

As a result, artistic practices in communist Poland likely differed from those described in Western literature. Because understanding an artwork’s materials and structure is essential for effective conservation, research has been undertaken to determine when and how synthetic binder-based paints were introduced into Polish painting. The study focuses on artworks created between 1955 and 1975, aiming to identify the materials used by artists and to reveal their studio practices and material choices during this period.

This paper presents the results of an ageing study performed on selected model samples, conducted as a preparatory stage to the broader technological investigation of artworks. The synthetic materials selected for the study represented different classes of binding media. As the most important and commonly found in paintings, the chosen groups included acrylic, alkyd, polyvinyl acetate (PVAc), and nitrocellulose [1] (see “Samples” section).

One of the aims was to obtain reference infrared (IR) spectra of paints that had undergone ageing, which would be useful for material identification in the subsequent stage of the project. In addition to expanding the reference library, the study aimed to monitor degradation processes in the examined materials, focusing on changes in their IR spectra, colour, and microscopic appearance during ageing. The results proved to be universally valuable to other researchers working on the conservation of modern and contemporary paintings.

Experimental

Samples

Materials selection

Titanium white was selected as the main pigment for all paints because its infrared spectrum does not interfere with the fingerprint region of the investigated synthetic binding media. Moreover, colour changes are more easily observed on white surfaces.

Among acrylic emulsion paints, Van Gogh and Amsterdam brands from Royal Talens (Netherlands) and System3 from Daler-Rowney (UK) were chosen, as both manufacturers were mentioned in interviews with Polish artists active during the investigated period [4-5]. Primal AC-33 mixed with titanium oxide using a spatula in a ratio of approximately 3:1 was also included to compare the behaviour of commercial artist paints with simpler formulations.

Several artists described the techniques used in their works as “polymer paints” [6] – most likely referring to vinyl emulsion paints – or “vinavil” [7], an adhesive made from polyvinyl acetate from VINAVIL (Italy). Therefore, the Maimeri Polycolor (Italy) artistic vinyl paint and Vinavil NPC were incorporated into the study.

Table 1. List of investigated products.

Commercial name	Manufacturer	Variant	Pigment	Product code	Binder medium
Van Gogh Acrylic Colour	Royal Talens (Netherlands)	Titanium White 105	PW6	22051050	p(nBA/MMA)
Amsterdam Standard Series Acrylic				17041050	
System3 Acrylic Paint	Daler-Rowney (UK)	Titanium White 009		D129059009	
Primal AC-33	Kremer Pigmente	-	-	75200	p(EA/MMA)
mixed with pigment		Titanium White Rutile	PW6	46200	-
Dekoral EMAKOL Strong	PPG Deco (Poland)	White Gloss RAL 9003	PW6*	11100PO012	alkyd
Jedynka Wood and Metal		White Gloss		320JRT0002	
Polycolor Fine vinyl colours	Industria Maimeri (Italy)	Titanium White 018	PW6	1202018	PVAc
Vinavil NPC Stella Bianca	VINAVIL (Italy)	-	-	9037735	
VIDARON Nitro Varnish	Śnieżka (Poland)	Clear Gloss	-	2100249501	nitrocellulose

*The manufacturer did not provide information on the pigment. Identification based on XRF analysis.

For alkyd and nitrocellulose binders, industrial coatings manufactured in Poland, by PPG Deco and Śnieżka, respectively, were selected. A complete list of materials, including manufacturers, binders, and pigments, verified by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray fluorescence spectrometry (XRF), is presented in Table 1 (see "Methods of analysis" for instrumentation details).

Preparation

Two film series were prepared by applying undiluted products onto glass plates with a metal spatula. The dried film thickness ranged from 0.1-0.2 mm for nitrocellulose varnish and alkyd enamels, and 0.6-0.7 mm for the other materials (Figure 1).

The samples were left to dry for seven days at room temperature before preliminary analyses were carried out using digital microscopy, XRF and ATR-FTIR. They were then left to cure for an additional five weeks prior to artificial ageing following the typical protocol reported in the literature [8].

Artificial ageing

Accelerated ageing was performed using a TestAn XENTEST 2200 chamber (Anticorr Gdańsk Agency, Poland). Samples were irradiated only in the dry phase with a xenon arc lamp. The radiation at 340 nm wavelength was 0.51 ± 0.02 W/m^2, and the total radiation dose reached 1.8 MJ/m^2 over a total exposure time of 1000 h.

Material stability was periodically assessed using ATR-FTIR spectroscopy and colour measurements (see "Methods of analysis") after 100, 200, 300, 500, and 1000 hours of UV exposure.

Methods of analysis

X-ray fluorescence (XRF)

Samples were analysed prior to ageing using a Skyray Genius 7000 Handheld XRF Spectrometer (Skyray Instruments, USA) with a 40 kV/100 μA excitation source to identify inorganic pigments and fillers. Two readings were collected for each sample, with a total acquisition time of 120 seconds per spot.

Digital microscopy

Observation of samples' surfaces using high-resolution digital microscopy was performed before and after ageing (1000 h of irradiation) using a Hirox 3D Digital Microscope HRX-01 (Hirox, Japan) with an HR-2500 zoom lens at magnifications of 140×, 400×, and 1000×, under both coaxial and side illumination. Images were processed with Hirox software.

Colour measurements

Colour was measured with a CM-2300d spectrophotometer (Konica Minolta, Japan) in the CIE 1976 $L^*a^*b^*$ (CIELAB). Three results were averaged for each sample [8].

In the CIELAB system, colour is described by three coordinates: L^* (lightness), a^* (green–red axis), and b^* (blue-yellow axis) [9]. Coordinates were measured before ageing and after 100, 200, 300, 500 and 1000 hours of irradiation. The total colour difference ($\Delta E*$) between subsequent stages was calculated using the formula [10]:

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

Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR was employed to identify the tested materials' chemical composition and monitor changes occurring during accelerated ageing [11]. Analyses were conducted using a Spectrum Two FT-IR Spectrometer equipped with a Universal ATR Sampling Accessory (PerkinElmer, USA). Spectra were acquired in a spectral range between 4000 and 400 cm$^{-1,}$ performing 16 scans at 4 cm^{-1} resolution. Data was processed using PerkinElmer Spectrum IR 10.6.2 software. Measurements were taken before ageing and after 100, 200, 300, 500, and 1000 hours of UV exposure.

Results and discussion

X-ray fluorescence

Analyses confirmed the presence of titanium white and chalk in all tested paints. In Jedynka and Dekoral enamels, Van Gogh and System3 acrylics and Polycolor vinyl paint, magnesium was also detected, most likely originating from dolomite or magnesium carbonate used as mineral fillers.

Both alkyd enamels contained small amounts of zinc and cobalt, probably resulting from the addition of zinc white and cobalt blue to enhance the optical properties of the paint.

In the case of Van Gogh Acrylic, although the manufacturer lists only titanium white (PW6) as the pigment, XRF analysis revealed significant amounts of zinc. This can be explained by the presence of lithopone, used as a filler, as indicated by the simultaneous detection of barium and sulphur.

Digital microscopy

Figure 1 shows a comparison of unaged and aged samples. Most of the changes in the microscopic image of the samples were connected with the accumulation of dirt and changes in colour, discussed in the “Colour change” section.

An exception was the Polycolor vinyl paint, in which short, narrow surface grooves appeared after ageing – features not present in any other tested material (Figure 2). Further investigation is needed to determine whether these grooves are specific to this product or represent a broader phenomenon.

Additionally, under coaxial illumination, industrial enamels exhibited a more complex surface structure, characterised by densely packed and generally smaller particles compared to artist paints (Figure 3). These differences may be attributed to the formulations of industrial coatings, which are designed for greater flowability, resulting in finer pigment and filler particles visible under coaxial light.

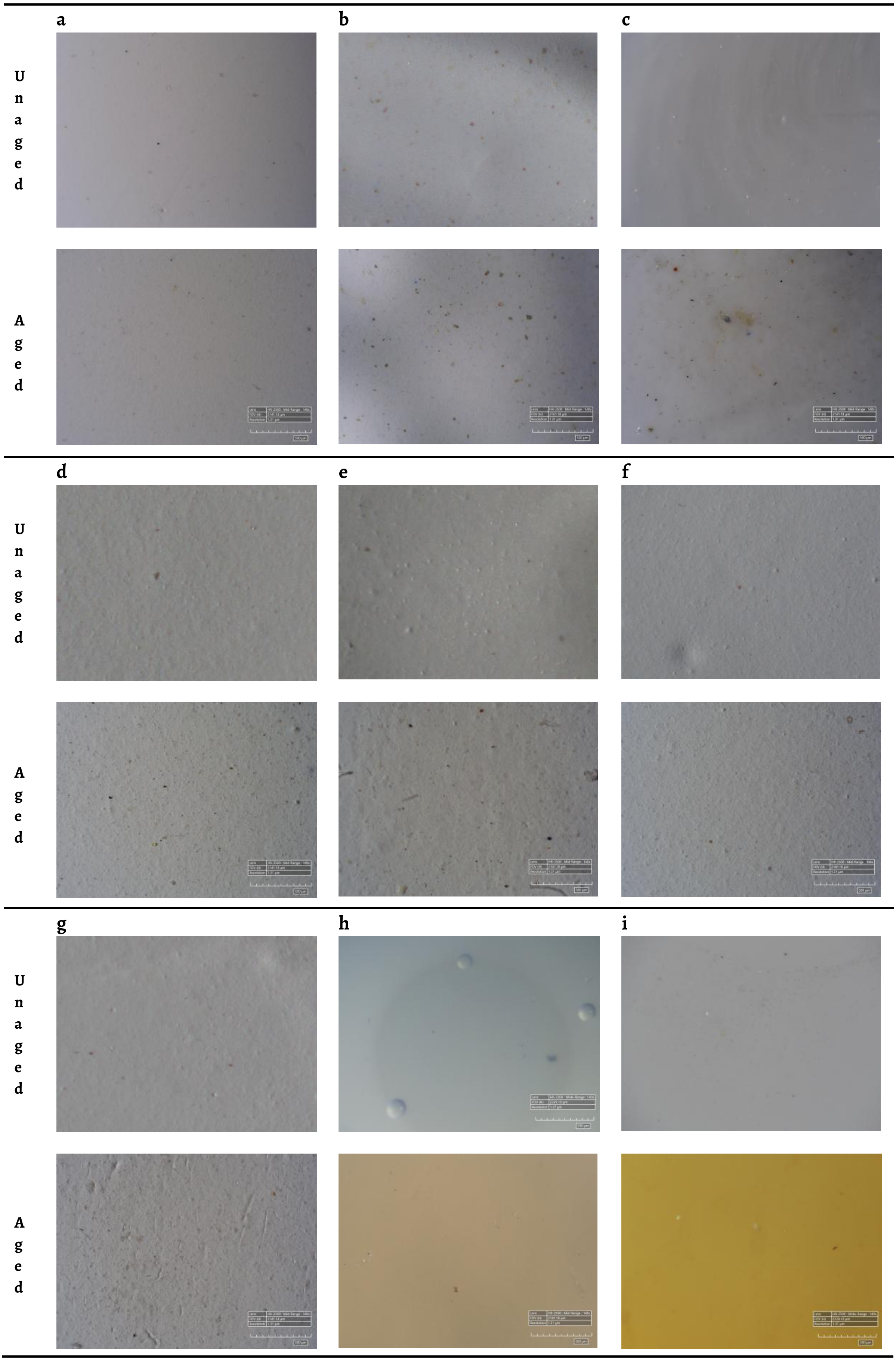

Figure 1. Microscopic images of unaged and aged samples: *a)* Jedynka; *b)* Dekoral Emakol; *c)* Primal AC-33with rutile; *d)* Van Gogh; *e)* System 3; *f)* Amsterdam; *g)* Polycolor; *h)* Vinavil; *i)* Vidaron.

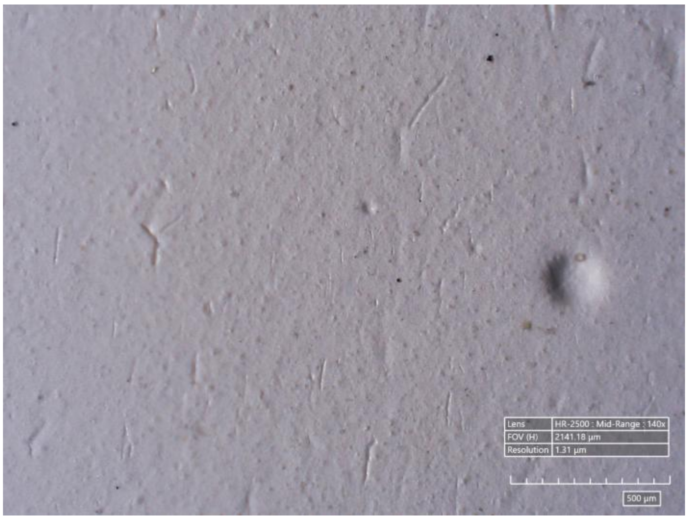

Figure 2. Digital microscopy (Hirox) images showing the surface of Maimeri Polycolor Fine Vinyl Colours in lateral illumination after ageing.

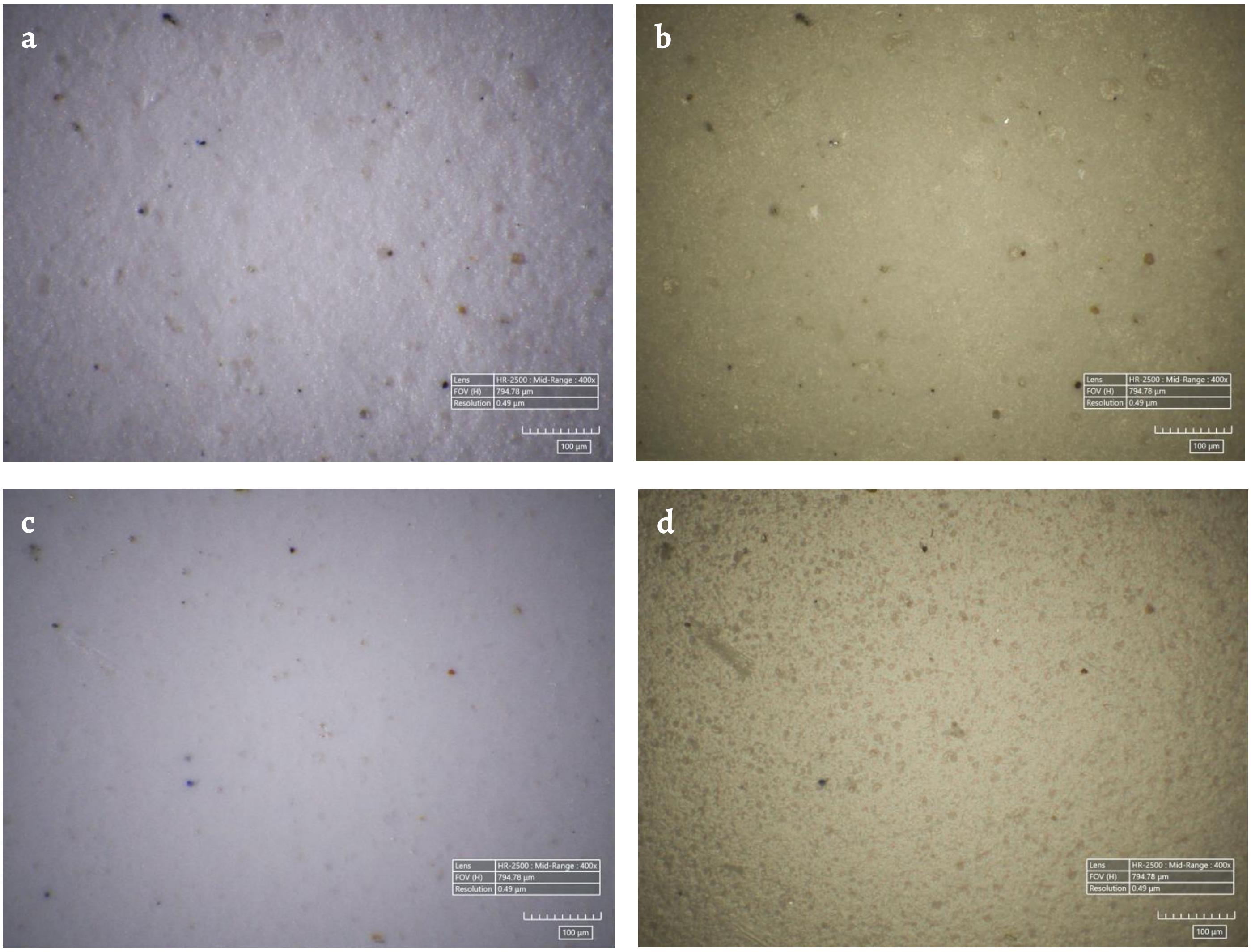

Figure 3. Digital microscopy (Hirox) images showing the surface of Daler-Rowney System 3 Acrylic in: *a)* lateral and *b)* coaxial illumination; and Jedynka alkyd enamel in *c)* lateral and *d)* coaxial illumination after ageing.

Colour change

The final results of the colour measurements are summarised in Table 2, which presents the shifts in lightness/darkness (ΔL^*), redness/greenness (Δa^*), yellowness/blueness (Δb^*), and total colour difference (ΔE^*) [12]. The values were averaged from two replicates of each material.

The obtained ΔE^* values can be interpreted according to the perceptibility of colour differences to a standard observer [9]:

- $0 < \Delta E < 1$ - observer does not notice the difference
- $1 < \Delta E < 2$ - only an experienced observer can notice the difference
- $2 < \Delta E < 3.5$ - an inexperienced observer also notices the difference
- $3.5 < \Delta E < 5$ - a clear difference in colour is noticed
- $5 < \Delta E$ - observer notices two different colours

The most significant colour changes were recorded for nitrocellulose lacquer and polyvinyl acetate dispersion, both exhibiting strong darkening and yellowing ($5 < \Delta E$). These effects are consistent with known degradation pathways for these polymers [13-14].

The four samples containing titanium white and acrylic binders showed slightly different responses to UV exposure. All exhibited initial brightening, most pronounced during the first half of the experiment, followed by partial recovery toward their original values. Among them, Amsterdam Acrylic showed excellent stability ($\Delta E < 1$). System3 Acrylic and Primal AC-33 mixed with rutile exhibited similar total colour changes ($2 < \Delta E < 3$), while Van Gogh Acrylic proved least stable ($\Delta E > 3.5$). Analysis of the individual coordinates suggests that the changes were primarily related to variations in L^* rather than b^*, indicating that lightness fluctuations, rather than yellowing, accounted for most of the observed differences.

Alkyd enamels exhibited ΔE values comparable to acrylics, but the change was mainly associated with negative Δb^* values, reflecting a shift toward cooler tones.

Polycolor vinyl emulsion paint showed total colour differences in the range of 3.5-5, comparable to the other commercial paints tested and indicating significantly greater stability than the clear polyvinyl acetate dispersion.

These findings suggest that the paint formulation as a whole, rather than the binder alone, plays a decisive role in colour stability. Pigments, fillers, extenders and other additives modifying product properties can significantly influence the photochemical resistance of synthetic paints [8, 13].

Table 2. Shifts in the L^*, a^*, b^*, and E^* coordinates after UV ageing.

Product	ΔL	Δa	Δb	ΔE
Jedynka White Gloss	-0.02	0.66	-1.92	2.03
Dekoral Emakol White Gloss	0.10	1.10	-3.42	3.59
Primal AC-33 with Rutile	1.63	0.24	0.42	2.74
Van Gogh Acrylic Titanium White	3.56	-0.03	0.37	3.58
System3 Acrylic Titanium White	0.86	0.14	-1.20	2.98
Amsterdam Titanium White	0.54	-0.01	0.22	0.58
Polycolor Titanium White	0.05	-0.01	-0.06	3.96
Vinavil NPC Stella Bianca	-4.12	1.68	10.22	11.37
Vidaron Nitro Varnish	-11.46	9.87	34.04	37.34

ATR-FTIR analysis

The most significant spectral changes observed in the examined materials are summarised in Table 3. As the influence of UV radiation was generally consistent within each binder type, the results are presented by class: alkyd (Figure 4), PVAc (Figure 4b), nitrocellulose (Figure 4c) and acrylic (Figure 4d).

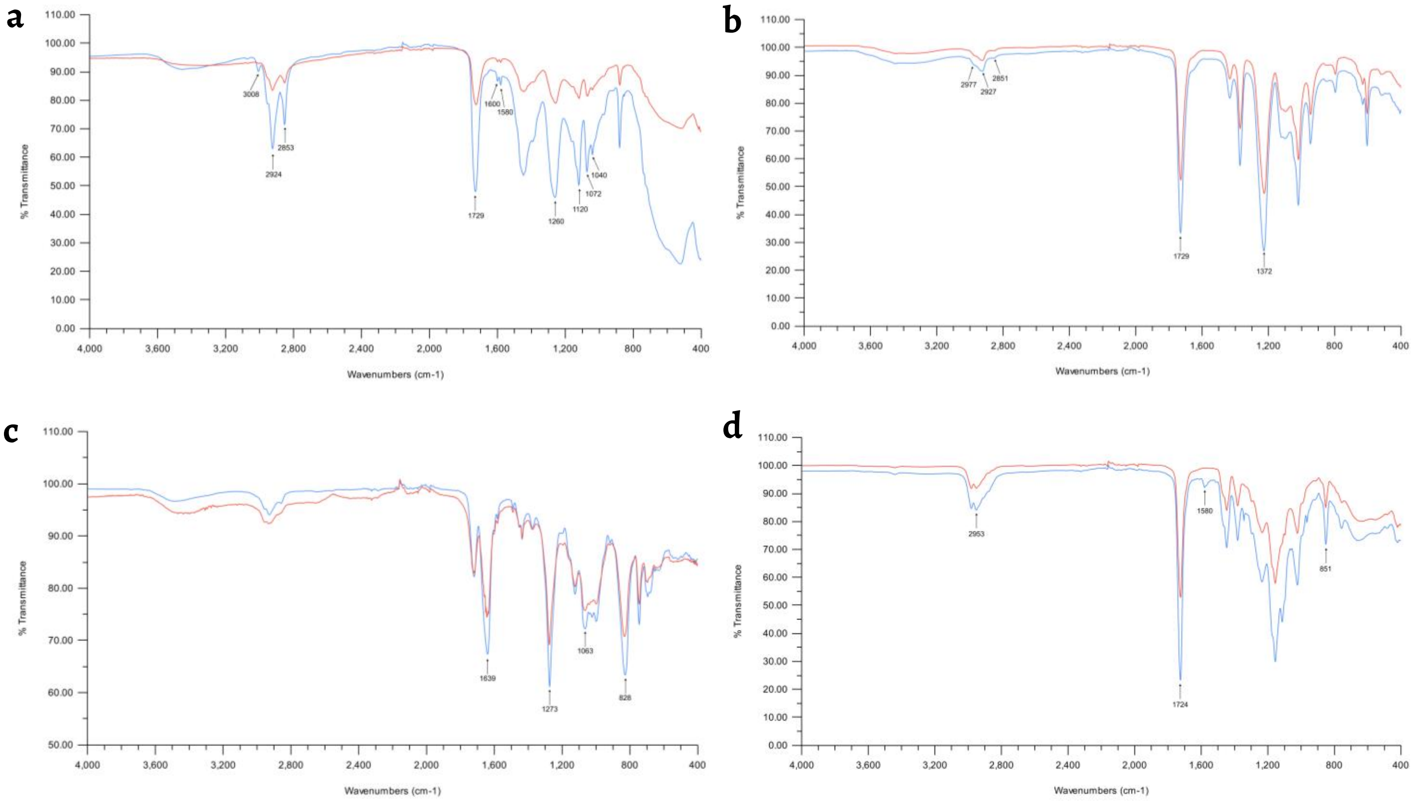

Figure 4. FTIR spectra before (blue) and after 1000 hours artificial ageing (red) of: *a)* Jedynka alkyd enamel; *b)* Vinavil NPC; *c)* Vidaron nitrocellulose lacquer; *d)* Primal AC-33 mixed with rutile.

Overall, differences between unaged and aged samples were more pronounced for the ready-made paints. The main exception was Daler-Rowney System3 Acrylic, whose spectrum remained almost unchanged after 1000 h of UV exposure (Figure 5).

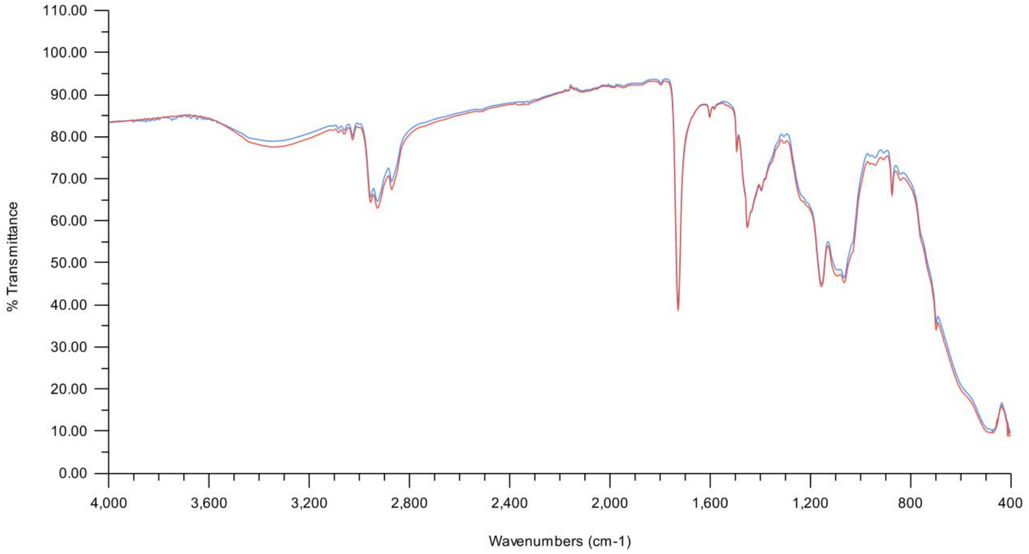

Figure 5. FTIR spectra before (blue) and after 1000 hours artificial ageing (red) of Daler-Rowney System3 Acrylic.

Table 3. Changes in the infrared spectra of the investigated materials, observed during the UV ageing.

Product	**Observed change**	**Timeframe of occurrence**	**Possible cause**
Alkyds			
	The peak at 3008 cm^{-1}, assigned to the vinyl proton of the C–H stretching [15], is no longer detectable	Within the first 100 h of irradiation	Decrease of the vinyl signal as the result of chemical curing [16]
	The gradual decrease in absorption of (C–H)CH$_2$ asymmetric stretching at 2925 cm^{-1}, symmetric stretching at 2855 cm^{-1} [17] and bending at 1446-1463 cm^{-1} [15], assigned to oil	Continuous through the ageing	Disappearance of methylene groups, possibly due to Norrish type I and II reactions [18] or oxidation of double bonds [12, 15].
	Reduction of the C=O carbonyl stretching absorption at 1729 cm^{-1} [17]		The loss of the ester group, probably due to the photo-Fries rearrangement [18]
	Progressive reduction in absorption of two peaks at 1600 and 1580 cm^{-1}, assigned to C=C stretching of the aromatic ring in the phthalic groups from the alkyd resin [17]		Lower amounts of free resin due to the progress of the cross-linking reactions [16]
	The gradual decrease in absorption of the phthalic C–O stretching band at 1260 and 1120 cm^{-1}		C-O bond scission and formation of the free ortho-phthalic acids from the carbonyl phthalic ester [12]
	Gradual decrease of the aromatic C–H in-plane deformation peaks at around 1071 and 1040 cm^{-1} [12]		Norrish type I reactions, leading to the formation of free phthalic acid [19]
Acrylics			
All	Gradual decrease in the –CH region at 3000-2800 cm^{-1}	Continuous through the ageing	Degradation of polymeric chains [20]
Van Gogh, System3, Amsterdam	Reduction of absorption in the -OH region (broad band centred at 3340-50 cm^{-1}) [20]		Oxidation processes [20]
Van Gogh, Amsterdam, Primal AC-33	Progressive decrease in intensity of the carbonyl group absorption at around 1727 cm^{-1} and in the ester region at 1155 cm^{-1} [20]		Side groups oxidation or elimination [20]
Primal AC-33	The disappearance of the peaks typical for PEG type surfactant at 1343, 1113, and 964 cm^{-1} [12]	Within the first 100 h of irradiation	Degradation of the ethoxylated chain and the hydrocarbon moiety [20]
	The disappearance of the peak at 1580 cm^{-1}		Evaporation or photodegradation of additives [8, 20]
Nitrocellulose			
	The nitrate group absorption peaks at 1639, 1273 and 828 cm^{-1} decreased during irradiation.	Continuous through the ageing	Progressive denitration of nitrocellulose [21]
	Reduction in absorptions of the broad band with a maximum at 1063 cm^{-1}		Chain scissions of acetal structures [21]
	The reduction in absorption of O–NO$_2$ bending vibrations at 745 at 695 cm^{-1} [22]		Photooxidation and the loss of the O–NO$_2$ group [21]
PVAc			
Polycolor Vinavil NPC	Continuous decrease of the absorptions in the 3000-2800 cm^{-1} region.	Continuous through the ageing	Degradation of the polymer chains [20]
	Gradual reduction of the carbonyl peak absorption at around 1730 cm^{-1}		Loss of the ester [12, 20] and the acetate group [20] due to the side group elimination.
	Decreasing intensity of the –CH absorption at around 1371 cm^{-1}		Degradation of the polymer chains [20]
Polycolor	Weak peaks at 1600 and 1587 cm^{-1} are no longer present	Within the first 100 h of irradiation	Loss of volatile additives, such as coalescing agents, during paint film curing [13, 20]

Conclusions

The UV photostability of nine commercial products containing acrylic, alkyd, polyvinyl acetate, and nitrocellulose resins - the four classes of synthetic binders most commonly found in twentieth-century paintings - was evaluated using colour measurements, ATR-FTIR spectroscopy, and digital microscopy.

Although this study does not aim to provide a comprehensive analysis of all degradation mechanisms affecting these materials, several noteworthy trends were identified. Despite variations in the total colour change (ΔE^*), all tested paints exhibited good resistance to yellowing, particularly when compared with nitrocellulose varnish and PVAc dispersion, both of which proved highly sensitive to UV radiation.

The ATR-FTIR analyses revealed distinct ageing behaviours among the four binder types. The majority of spectral changes can be attributed to polymer chain scission and oxidation processes, leading to gradual decreases in absorption intensity. In the case of the alkyd, Primal AC-33, and Polycolor samples, the disappearance of specific peaks associated with curing was observed. These findings emphasise the importance of recording reference spectra not only for unaged materials but also for aged ones, which more accurately represent the condition of historical paint films.

Digital microscopy did not reveal significant morphological alterations resulting from ageing. However, a correlation between the flowability of paint and its appearance under coaxial illumination was noted, suggesting potential diagnostic value for distinguishing between artistic and industrial formulations.

The research did not indicate a single appropriate method for the identification of materials or the determination of ageing markers. However, it represents an important step forward in gathering subtle factors that may support a deeper recognition of modern synthetic media used by artists. The findings suggest that, in the future, some paints could be distinguished using fully non-invasive portable instrumentation. Nevertheless, this stage must first be preceded by the continued development of a comprehensive identification methodology, based on invasive analyses of model samples, to establish a solid foundation for future, ideally non-destructive, assessments of paintings

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