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# Shrinkage and mechanical properties of drying oil paints

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## **Abstract**

Understanding how the evolving molecular composition of an oil paint layer on its transition to an aged solid film affects its dimensional change and mechanical properties is fundamental to the assessment of material durability and more broadly risk of degradation of oil paintings. Tensile properties—modulus of elasticity and strain at break—as well as cumulative shrinkage were determined for a selection of oil paints from Mecklenburg's Paint Reference Collection now after approximately 30 years of drying. The oil paints were found to get stiffer and more brittle with diminishing plastic deformation and increasingly elastic behaviour. For some paints, the increases in stiffness and decreases in the strain at break were dramatic during the late stage of drying. The observations modify the current physical model of paintings in which the mismatch in the response of glue-based ground layer and unrestrained wood or canvas support to variations in relative humidity (RH) has been identified as the worst-case condition for the fracturing of the entire pictorial layer. This study demonstrated that some paints were more brittle than the glue-based ground layer and as a consequence more vulnerable to cracking. The shrinkage of paints due to molecular relocation and/or evaporation of organic medium as they dry and age was measured. This shrinkage can exceed their strain at break and lead to fracturing of the oil paint layer if it is restrained by a dimensionally stable substrate. Consequently, after long-term drying, the cumulative shrinkage can cause oil paints to crack even in absence of fluctuations in RH or temperature. An example of cracking developed in an oil paint layer on the top of an undamaged ground layer in a historic panel painting was made evident by the X-ray microtomography.

Keywords: Oil paints, Drying, Mechanical properties, Shrinkage, Cracking, Paintings

## Introduction

Drying oils used as binders in oil paints are glycerolipids based predominantly on polyunsaturated fatty acids. Drying oils solidify and harden through chemical reactions with oxygen, entailing two main paths—oxidation and crosslinking [1]. All paints show a rapid initial oxygen uptake followed by mass loss due to the decomposition of oxygenated compounds with low-molecular-weight molecules lost by evaporation [2]. Crosslinking is fundamental in the formation of a durable paint film and the degree

of crosslinking and types of crosslinks promoted by different pigments are important contributors to the long-term chemical and mechanical stability of the oil paint layer. In parallel to oxidation, hydrolysis of ester bonds takes place yielding di- and monoglycerides and free fatty acids. Metal ions released from pigments and additives, that improve the optical properties and workability of the paint, react with free fatty acids to form metal soaps or with carboxylic groups present in the cross-linked polymer transforming it into an ionomer. As a result, the molecular composition of the oil binder evolves from the initial mixture of primarily polyunsaturated triglycerides to a complex system of the dominant cross-linked ionomeric network, free fatty and dicarboxylic acids, metal soaps, as well as mono-, di- and triglycerides. The recent

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solid-state Nuclear Magnetic Resonance (NMR) study demonstrated that the cross-linked network constituted about 88% of the cured binder in a paint comprising blue ultramarine and linseed oil [3].

Understanding how the evolving molecular composition of an oil paint layer on its transition to an aged solid film affects its dimensional change and mechanical properties allows not only the durability of the layer itself to be assessed but a broader mechanism of degradation in oil paintings to be comprehended. They are complex multi-layered structures composed of wooden or canvas support that were often sized with animal glue, a ground preparatory layer, and paint and varnish layers on the top. Materials building up the structure swell on absorbing moisture when the ambient relative humidity (RH) increases or shrink on losing moisture when RH decreases, with the exception of shrinkage in the linen canvases which can be observed at high RH levels. The moisture content in each material eventually attains a constant level at a given temperature and RH-termed the equilibrium moisture content—and, in consequence, the related 'equilibrium' dimensions. The constraint from that moisture-related dimensional changes, on account of rigid construction, as frames, stretchers, strainers or cradles, or a connection to materials that respond differently, induces stresses in the layers which can cause deformation, cracking, and delamination [4]. Paintings are often dominant in museum collections and tight environmental controls are generally seen as a way to reduce the risk of damage, which involves energy-intensive airconditioning systems. Scientific understanding of how changes in environmental conditions affect paintings is therefore a pathway to the development of more sustainable climate control guidelines in museums and heritage

Compiling material parameters for oil-based pictorial layers presents a challenge as they are known to evolve over years and might continue to evolve even over centuries. A recent review listed 18 studies carried out over the last three decades which used uniaxial tensile testing to systematically measure the mechanical properties of naturally cured oil paints [5]. Most of the studies were conducted by Mecklenburg and his collaborators at the Smithsonian Institution or used specimens currently belonging to Mecklenburg's Paint Reference Collection at the Smithsonian Museum Conservation Institute ([6], p. 137-71), [7-11]. The paint films were cast from 1978/9until the late 1990-ies on polyester sheets and were stressstrain tested in different moments of their drying process spanning up to 35 years. The tests allowed the evolution of changes in the mechanical properties as a function of pigments and binders present in their composition to be captured. Paints with basic lead carbonate—lead white—are known to form tough and durable films which were found to get stiffer and stronger with the time and hence be chemically active even after 18 years of curing [9]. The increase in stiffness and strength was accompanied by a modest reduction in the strain (elongation) at break that is to say the aged paints preserved their considerable flexibility. In turn, the time-induced increase in stiffness and strength of paints containing zinc oxide was accompanied by a severe reduction of their strain at break making the paints extremely brittle. In contrast, oil paints containing raw and burnt umber pigments with iron oxides appear to form durable films initially, but they experience a serious loss of strength and stiffness combined with increasing plasticity as curing time goes on and early hydrolysis reactions take place [9, 10].

Mecklenburg et al. observed for paint films of lead white in cold-pressed linseed oil that the relationship between stress at a specific strain measured and the natural logarithm of curing time of up to 10 years is linear [7]. In this way, stress-strain curves were predicted for films of any age. The extrapolation indicated that the paint film properties change very slowly after about 50 years and paint films several hundred years old might not be substantially stiffer or more brittle than films only decades old [8].

The aim of the present study has been to obtain further information on the effects of a selection of pigments on the mechanical properties of naturally aged paints from Mecklenburg's Paint Reference Collection now after approximately 30 years of drying. Further, cumulative shrinkage of the films during these long-term film-forming processes was measured. The cumulative shrinkage is related to the evolution of the molecular composition of the oil binder, especially evaporation of low-molecular-weight organic components, and subsequent diffusing out free volume locked in the material until the equilibrium state. This shrinkage may engender stresses and lead to the formation of crack systems in the paint layer.

# **Materials and methods**

The oil paint films investigated in this study (Table 1) come from Mecklenburg's Paint Reference Collection at the Smithsonian Museum Conservation Institute and represent common paints used throughout history in the production of easel paintings, from traditional (lead white, verdigris, malachite, red iron oxide, sap green) to more contemporary ones (zinc white, synthetic ultramarine). They belong to a group of 'control paints' and all were specifically manufactured by Gamblin Artists' Oils Co. with pigments ground in the same cold-pressed linseed oil (CPLO) both the pigments and the oil from Kremer Pigments Inc. Litharge, a natural mineral form of lead (II) oxide, was added as a drier to one of the

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Table	1 Dotaile	of oil paint	invoctiontod	all made with	cold proces	lincood oil
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Pigments and driers	Size [mm]	Thickness [µm]	PVC <sup>a</sup> [%]	Date of casting
Lead white	20 × 12	130	44	07.02.1990
Lead white with litharge	18 × 9.5	140	44	06.02.1990
Zinc white	24 × 8.5	260	35	04.12.1998
Sap green	26 × 17	280	=	11.12.1998
Verdigris	18 × 10	420	53	25.01.1999
Red iron oxide	21 × 10	190	12	01.06.1992
Malachite	25 × 15	290	48	15.03.1990
Synthetic ultramarine	15 × 12	340	45	13.05.1992

<sup>&</sup>lt;sup>a</sup> Pigment volume concentration, PVC = P/(P + B) where P and B are volumes of the pigment and the oil binder, respectively

specimens with lead white. Thin layers of paints were cast in the 1990s on polyester sheets and allowed to dry under controlled environmental conditions of room temperature and the 40–50% RH range until 2005 from when they were stored in room conditions with no RH control.

The most recent tensile properties were determined using a Universal Testing Machine (UTM) from Hegewald & Peschke MPT GmbH (Nossen, Germany) equipped with video extensometer ONE. Prior to the test, each specimen investigated was stored in the laboratory at temperature ranging between 23 and 25 °C and approximately 50% RH. As some paint specimens arched upwards in the middle, they were straightened by storing at 50 °C and 50% RH from one to seven days. After the procedure, they were stored in the laboratory for at least 10 days. Elevating temperature alters paint films to more rubbery materials and facilitates the removal of distortions. Earlier experiments demonstrated that exposing oil paint specimens at 50 °C for less than 10 days does not alter their properties at the test conditions [12]. As the specimens are brittle or soft, they were secured from damage during mounting in UTM by placing their edges in moulds into which epoxy resin was poured to harden into extended specimen ends. Specimens secured in this way were safely mounted in UTM. The rate of elongation was 0.125 mm/min corresponding, for the specimens about 20 mm long, to a strain rate of approximately  $1 \times 10^{-4}$  mm/mm s<sup>-1</sup>. The mechanical properties of artist paints are profoundly affected by strain rate. As the aim of the study has been to compare the mechanical properties of paint films from Mecklenburg's Paint Reference Collection measured now and in the earlier years of their drying process, the strain rate adopted corresponded to that in earlier 'rapid loading' experiments in which strain rate ranged between  $1 \times 10^{-3}$ and  $1 \times 10^{-5}$  mm/mm s<sup>-1</sup> ([6], Fig. 5). In particular, the strain rate adopted was close to  $0.4 \times 10^{-4}$  mm/ mm s<sup>-1</sup> calculated from the conditions of 30-s relaxation tests which were predominantly used in the earlier rapid loading experiments. In the tests, the paint specimen was rapidly strained a small amount, approximately  $1.2 \times 10^{-3}$  mm/mm, in a manual tensiometer and was allowed to stress relax for 30 s before it was subjected to a subsequent strain increment.

Dimensional change was measured by recording positions of eight pairs of reference points applied with a black or white marker depending on specimen colour, using the optical extensometer. Four pairs were evenly distributed across the specimen width, typically at a distance of 2 mm from the UTM handles, the other four pairs were marked in the middle of the specimen length. The strain was calculated as an average of four measurements unless recorded values were corrupted due to loss of reference point recognition. Poisson's ratio was determined by measuring the sample deformation in the directions along and across the load application, using four pairs of reference points in each direction.

As most paint films investigated adhered to polyester sheets on which they had been cast, a modified ASTM D6911-17E standard was used to measure internal stresses engendered in the paint films by shrinkage which had occurred during the long-term drying process [13]. The stress is determined from the measurement of the deflection of the coating-substrate system:

$$S = \frac{hE_{s}t^{3}}{3L^{2}c(t+c)(1-\gamma_{s})} + \frac{hE_{c}(t+c)}{L^{2}(1-\gamma_{c})},$$

where S is the internal stress, h is the measured deflection,  $E_s$  and  $E_c$  are the moduli of elasticity of substrate and coating, respectively,  $\gamma_s$  and  $\gamma_c$  are the Poisson's ratios of substrate and coating, respectively, L is the length of the substrate between the points of contact, t and t are thicknesses of substrate and coating, respectively.

The deflection of a specimen was measured with the use of a Micro-Epsilon optoNCDT distance laser detector operated with 670 nm wavelength (Fig. 1). Values of  $E_s$ ,  $E_c$ ,  $\gamma_s$  and  $\gamma_c$  were obtained from the measurements of

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tensile properties described above. The length between the points of contact was 18 mm. The thicknesses of the coating and substrate were measured using a micrometer screw.

Shrinkage  $\epsilon$  accumulated in a given oil paint film was then calculated:

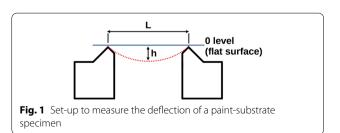
$$\epsilon = \frac{S(1 - \gamma_c) * 100}{E_c}.$$

Computerized microtomography data were collected on a RXSolutions EasyTom 150–160 tomograph as described in [14]. The tomograms were recorded with a voxel size of 2  $\mu$ m.

#### **Results and discussion**

## **Tensile properties**

The moduli of elasticity were determined from the slope of the load-extension curves at low strains not exceeding the level of 0.005, so they represent approximately the initial stiffness of the paints. Poisson's ratios were calculated as the negative ratio of slopes of the linear fit to the linear part of strains in the directions across and along the load application. The moduli of elasticity, Poisson's ratios and strains at break determined from the tensile tests are listed in Table 2; two values are provided for lead white, zinc oxide and verdigris for which enough material was available. It should be born in mind that strain is defined as the change in length divided by the specimen's original length. Owing to the exceptional scientific value of materials from Mecklenburg's Paint Reference Collection, the research team decided to perform the destructive tensile tests on the specimens merely approximately 20 mm long (Table 1). In consequence, the measured elongation increments on loading were very small, especially for brittle specimens which failed at low strains. Further, the 30-year old paint films were to varying extent distorted and the straightening procedure described in the "Materials and methods" section did not produce ideally planar specimens. The two factors resulted in increased uncertainty of strain measurements reflected by scattering of two test results: insignificant in the case of flexible paint with lead white but increasing for extremely brittle pains with zinc oxide and verdigris. In spite of the significant



uncertainty of a single measurement of tensile properties of brittle paints, the results are listed in Table 2 as they indicate tendencies in evolution of paint film properties with the drying time.

Using the published results of the tensile testing of the same paint samples in the earlier years of their drying process, changes occurring during the last 21-32 years (depending on the paint) in the mechanical properties of the paint films investigated were analysed. Changes in stress-strain curves of the lead white paint, which is known to form tough and durable films, are shown in Fig. 2. The paint continues to get stiffer and stronger after now 30 years of drying under laboratory conditions indicating that the molecular system is continually evolving, the ageing process is chemically driven and is not the result of exposure to an adverse environment. The increase in stiffness is accompanied by a reduction in the strain at break. As the paint gets older, plastic deformation diminishes and the paint exhibits a marked elastic range at low strain. The strain at which the stress-strain curves begin to deviate from a straight line and which is assumed to represent the upper limit of the elastic range is 0.0015 for paints dried for 18.75 and 30 years.

Further, four white and green paints show changes in stiffness with the drying time similar to those experienced by the lead white paint (Fig. 3). It is worth noting that data in Figs. 3 and 4 plotted with full circles were obtained for the same paint specimens tested at different moments of their drying process using the same rate of strain application of approximately  $1 \times 10^{-4}$  mm/mm  $s^{-1}$  so they are fully comparable. Data on other paints with lead white and zinc oxide mixed with the coldpressed linseed oil reported in the literature are shown with other symbols for comparison to illustrate specimen-to-specimen variability. Paints in the group shown in Fig. 3 exhibited considerable stiffness after the initial drying exceeding one year and the parameter continued to increase with the drying time, dramatically in the case of lead white with litharge the modulus of elasticity of which abruptly increased to almost 3000 MPa after 30 years of drying. This demonstrates that driers such as litharge used to accelerate drying of an oil paint film can have also a significant impact on its long-term mechanical performance.

In contrast, paints with synthetic ultramarine and malachite shown in Fig. 4 had comparatively low initial stiffness which dramatically increased during the late stage of drying. Only the red iron oxide paint experienced a small increase in stiffness as shown in the same figure. Furthermore, increases in stiffness observed in paints containing iron oxide or ultramarine followed the initial loss of stiffness due to early hydrolysis reactions taking place.

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Table 2 Elasticity modulus, Poisson's ratio, strain at break and cumulative shrinkage of the oil paints investigated

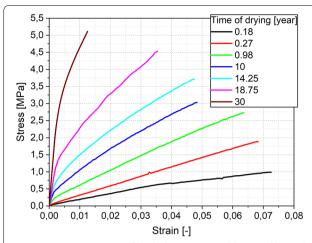
Pigments and driers	Drying time [year]	Modulus of elasticity [MPa]	Poisson ratio [-]	Strain at break [10 <sup>-2</sup> ]	Cumulative shrinkage [10 <sup>-2</sup> ]	Source
Lead white	0.2	18		7.3		[9, 15]
	0.3	34		6.8		
	1	110		6.4		
	10	210		4.8		
	14.2	370		4.7		
	18.7	430		3.6		
	15	270		2.0		[10]
	31	970, 1080	0.3, –	0.8, 1.5	0.5	This study
Lead white with litharge	0.2	41		2.0		[9, 15]
•	0.3	120		5.0		
	1	280		3.2		
	10	430		2.6		
	16.7	650		1		
	15	660		1.8		[10]
	31	2900	0.5	0.5	0.9	This study
Zinc white	8	450		2.0		[16]
	8	670		1.3		[9, 15]
	9.5	370				
	15	700		0.3		[10]
	23	2000, 3000	0.5, –	0.1, 0.3	0.3	This study
Sap green	1.2	110		2.4		[15]
. 3	7.4	310		1.4		
	14.2	510		0.8		
	23	730	0.5	0.75	0.3	This study
Verdigris	1.25	670		0.6		[15]
,	7.5	1800		0.2		
	21	1100, 2800	0.6, 0.5	0.1, 0.1	1.7	This study
Red iron oxide	1.25	11		11		[15]
	7.5	4.0		7.1		
	29	50	0.3	2.8	No shrinkage	This study
Malachite	1.25	99				[15]
	7.4	260		1.8		
	14.2	190		3.4		
	22	3300	0.5 <sup>a</sup>	0.2	0.8	This study
Synthetic ultramarine	1.25	140		2.6		[15]
,	1.5	96				
	7.5	9.0		3.9		
	29	1400	0.2	0.4	Not determined	This study

<sup>&</sup>lt;sup>a</sup> Value assumed due to similarity of moduli of elasticity of malachite and lead white with litharge

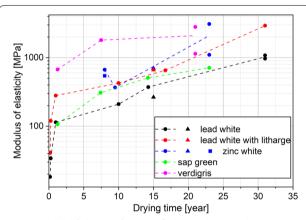
The increase in stiffness observed for all paints were accompanied by reduction in the strain at break indicating continuous embrittlement of the paints with the drying time (Fig. 5).

The values of strain at break determined in this study for oil paints dried for a relatively long time modify and refine the current laminar structural model of the assembly of the layers that constitute easel paintings subjected to variations of RH [4]. The model is based on the principle of superposition and assumed that the overall structural response of a painting is obtained by superimposing individual responses of all components together. Upon variations in RH, the wood or canvas support undergoes dimensional change, inducing strain in all layers that constitute the structure of the pictorial layer: animal glue size, a preparatory ground layer, paint and varnish

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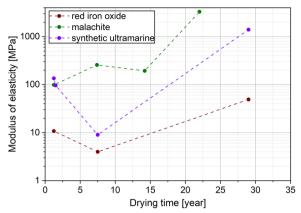


**Fig. 2** Stress-strain curves of lead white paint in cold-pressed linseed oil after increasing time of drying; data from [9] and this study—the specimen dried for 30 years

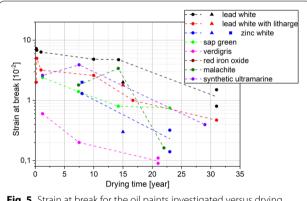


**Fig. 3** Moduli of elasticity for a set of white and green oil paints versus drying time; filled circles—data from [9, 15] and this study—the specimens older than 20 years, triangles—data from [10], a square—data from [16]

layers on the top. So far, a glue-based ground layer – a mixture of animal glue and white inert solid, 'the pigment', has been considered the component of the pictorial layer that has the lowest strain at break and cracks first when the strain generated in the layer increases [4]. The strain at break of glue-based ground was determined to be around 0.002 at the RH mid-range in studies of usable grounds with PVC values ranging between 85 and 95% - PVC = P/(P+B) where P and B are volumes of the pigment and the dried glue binder in this case. Such preparations match grounds commonly used to produce or restore paintings as freshly prepared glue-based grounds are known to dry and stabilize quickly ([6], p. 173–217, [17, 18]). This study demonstrated that some



**Fig. 4** Moduli of elasticity of the oil paints with red iron oxide, malachite and synthetic ultramarine versus drying time; data from [15] and this study—the specimens older than 20 years



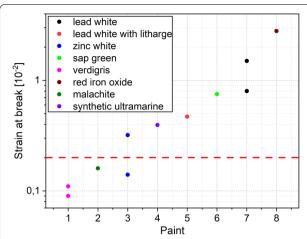
**Fig. 5** Strain at break for the oil paints investigated versus drying time; sources of the data as in Figs. 3 and 4

paints might be more brittle than the glue-based ground and in consequence crack first when the pictorial layer experiences strain due to the swelling or shrinkage of the painting (Fig. 6).

#### **Cumulative shrinkage**

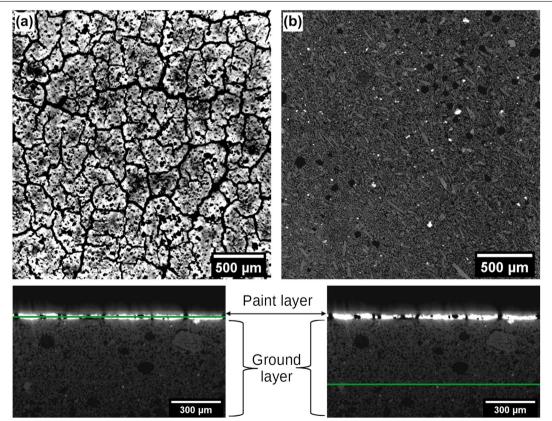
The paints experienced a cumulative drying shrinkage the values of which are listed in Table 2. The paint with red iron oxide did not show any shrinkage. In the remaining paints, the shrinkage varied from 0.3% (sap green and zinc oxide) to 1.7% (verdigris). Cumulative shrinkage exceeding the strain at break can lead to fracturing of the oil paint layer if it is restrained by a dimensionally stable substrate. Shrinkage approaching or exceeding the strain at break was observed for four paints. In turn, the paint with lead white exhibited moderate drying shrinkage combined with comparatively high strain at break, making it resistant to cracking at this stage of drying.

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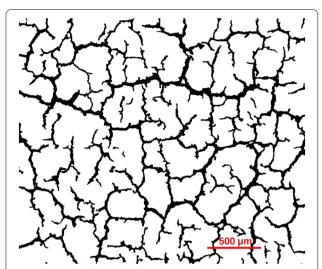
**Fig. 6** Strain at break for the oil paints investigated. Strain at break of 0.002 characteristic of the glue-based ground is marked with a red dashed line

The observations indicate that cracking may develop in oil paint layers independently of fractures in the ground layers and be independent of the moisture response of the supports. Further, shrinking paints tend to bend and lift away from the substrate, which increases the risk of delamination and loss of paint. An example of such cracking mechanism was revealed in a specimen of panel painting dated to the 17th century with the use of X-ray computer microtomography (Figs. 7, 8). The microscopic analysis showed that the paint layer is composed of a white material containing blue particles randomly distributed in the paint. The ground layer was also white but of a darker shade. The analysis performed using the X-ray fluorescence (XRF) revealed lead in the paint layer indicating that it is rich in lead white whereas calcium was identified in the ground indicating the presence of chalk



**Fig. 7** X-ray microtomographs of pictorial layer in a historic panel painting; cross-sections parallel to the surface: **a** paint layer, **b** ground. For presentation, the X-ray absorbing material is represented on a grey scale in which white and black colours correspond to highly and least absorbing materials, respectively. The black spots in the X-ray microtomograph of the paint layer correspond to grains of the blue pigment, most probably natural ultramarine

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**Fig. 8** Binarized image of the crack pattern extracted from the X-ray microtomograph shown in Fig. 7a with manually removed spots of the blue pigment

or gypsum typical inert solids used to produce grounds in the 17th century [19].

The analysed fragment had dimensions of 2.2 mm x 2.2 mm. Analysis of the crack pattern in the oil paint layer was performed using ImageJ software [20]. The crack system is composed of irregular 'cracked mud' paint islands without any relation to the anatomical directions of the wood substrate. Such random crack orientation indicates drying shrinkage of the paint as the source of stresses that are the same in all directions and independent of any other layers or the wood substrate. Approximately, 100 paint islands were identified in the analysed fragment. Assuming their square shape, the area of a paint island is 0.04 mm<sup>2</sup> and the equivalent distance between cracks 0.2 mm. Total coverage by the paint is approximately 82% and the remaining part is covered by cracks. The mean width of cracks calculated from 56 readings is  $20 \pm 8 \mu m$ . The linear shrinkage of the paint after more than 400 years of drying was estimated to be 9% as such shrinkage results in coverage of 82%. The shrinkage is much greater than strains induced by any wooden substrate responding to even extreme RH variations.

A question arises at this point as to the risk of further cracking of the paint layer due to tensile loading engendered either by possible continued paint shrinkage or the moisture response of the wooden substrate caused by environmental instabilities. In the laminar structures, new cracks develop in the middle between two existing cracks as in this area tension engendered by loading reaches the maximal value. If the strength of the material is exceeded, a new crack nucleates. When the distance between cracks decreases below a certain critical value,

any additional stretching does not initiate new cracks. The stress in the centre between two adjacent cracks is no longer tensile but becomes compressive [14, 21]. The critical distance between cracks at which no new cracks form depends on the thickness of the fracturing layer. Therefore, the critical ratio of the distance between cracks to layer thickness at which stress in the midpoint between cracks drops to zero is determined as the indicator that crack saturation is attained in the layer.

Taking into account the paint layer thickness of  $33\pm6~\mu m$  calculated from 184 readings, the ratio of the distance between cracks to the thickness of the paint layer is approximately 6. This value agrees well with the prediction of 3D modelling performed for the animal glue ground layer on wood [22]. The ground had a stiffness of 3750 MPa close to that of aged oil paints as revealed in this study. The modelling established that, for such material, the critical ratio of the distance between cracks to the thickness of the fracturing layer is typically between 3.5 and 5. Therefore, it can be concluded that crack network in the paint layer analysed has attained saturation or is close to it, which makes the layer significantly less vulnerable to further cracking.

#### **Conclusions**

The most general conclusion from this study is that oil paints continue to get stiffer and more brittle after now 30 years of drying under laboratory conditions, which indicates that the paint molecular system is still evolving. As the paint gets older, plastic deformation diminishes and the elastic behaviour becomes more prominent. Contrary to earlier predictions, the evolution of paint film properties did not slow with the drying time and dramatic increases in stiffness and decreases in the strain at break were observed during the late stage of drying for some paints.

The observations modify the current physical model of paintings in which the mismatch in the response of glue-based ground layer and wood or canvas substrate to variations in RH has been identified as the worst-case condition for the fracturing of the entire pictorial layer. This study demonstrated that some oil paints could be more brittle than the ground layer and in consequence more vulnerable to cracking.

The cumulative shrinkage observed for some paints may exceed the strain at break and lead to fracturing of the oil paint layer if it is restrained by a dimensionally stable substrate. In consequence, after long-term drying, the cumulative shrinkage can cause oil paints to crack even in absence of fluctuations in RH or temperature. This implies that even in the most tightly controlled environments in museums, cracks cannot be avoided for these paints. An example of cracking developed in an oil paint

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layer on the top of an undamaged ground layer was made evident by the x-ray microtomography.

The observations have implications for understanding paintings as physical systems and advancing appropriate environmental specifications for painting collections. The specifications cannot be derived using the criterion of crack initiation in undamaged layers building laminar structures of paintings. The developed crack networks need to be considered as paintings become less and less vulnerable to stresses generated by environmental instabilities when crack density increases. Computer modelling which simulates 'real-time' moisture movement and the resulting strain and stress fields across paintings is an effective way of analyzing their structural response under environmental loading if tensile properties of cracked rather than undamaged layers are used. An alternative approach may rely on large-scale surveys of museum collections of similar and well-defined paintings (collection analysis) to establish the harmlessness of the existing climatic conditions or trace new damage accumulating in paintings, obtaining thus evidence necessary to inform climate specifications.

#### **Abbreviations**

CPLO: Cold-pressed linseed oil; NMR: Nuclear magnetic resonance; PVC: Pigment volume concentration; RH: Relative humidity; UTM: Universal testing machine; XRF: X-ray fluorescence.

# Acknowledgements

The authors are grateful to Patrick Kékicheff, Damien Favier and Łukasz Bratasz for the X-ray micro-fluorescence analysis of a specimen of panel painting conducted at synchrotron SOLEIL. Full information on the study will be contained in the forthcoming publication.

#### **Author contributions**

CKA, MS, ŁB conceived the research hypotheses, ŁB planned research methods and experiments, LFL and MFM prepared the specimens, AJ carried out the measurements of mechanical properties and drying shrinkage, PK and DF carried out µXCT measurements, AJ, RK, ŁB analysed and interpreted results, RK wrote the first draft of the manuscript. All authors discussed the research outcome, as well as developed and approved the final manuscript.

#### Funding

This work was funded by the European Union's Horizon 2020 research and innovation program under grant agreement No. 814624 and the statutory research fund of the Jerzy Haber Institute of Catalysis and Surface Chemistry Polish Academy of Sciences. Łukasz Bratasz's work was financed by the Polish National Agency for Academic Exchange, project Polish Returns [Grant PPN/PPO/2018/1/00004/U/00001].

# Availability of data and materials

All data needed to evaluate the conclusions in the paper are present in the paper. Additional data related to this paper may be requested from the corresponding author.

#### **Declarations**

#### **Competing interests**

The authors declare that they have no competing interests.

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Received: 12 July 2022 Accepted: 8 October 2022 Published online: 03 November 2022

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