# Conservation issues of modern oil paintings: a molecular model on paint curing

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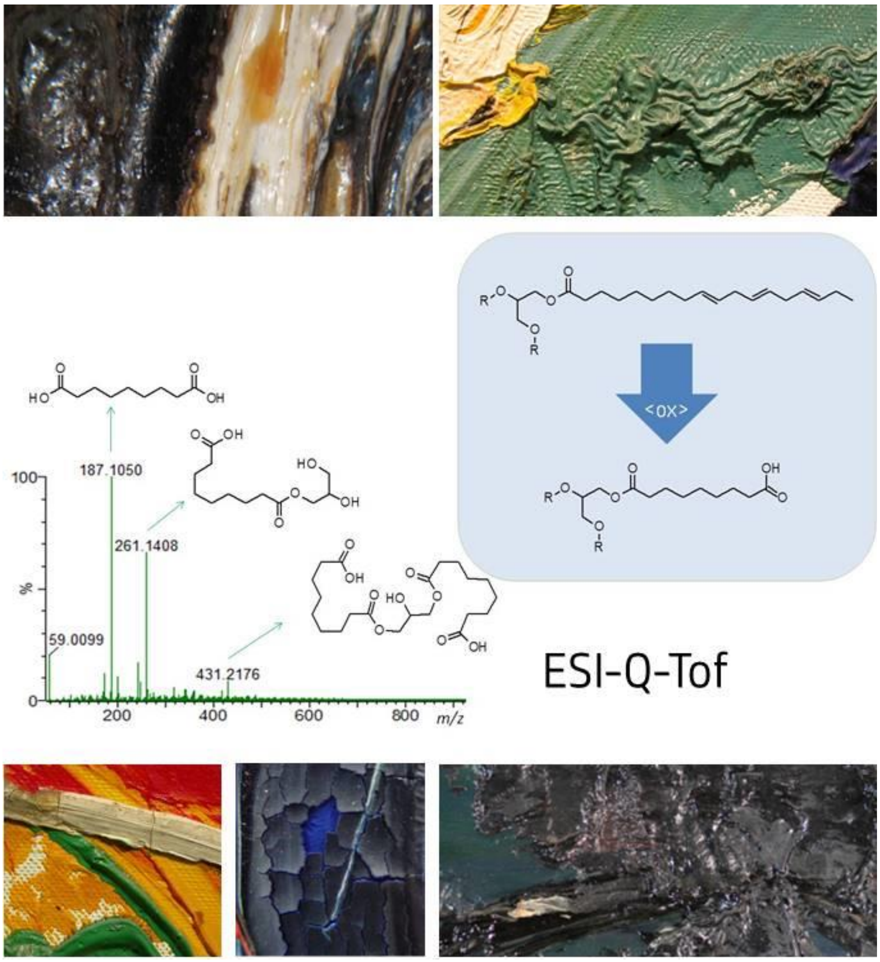
CONSPECTUS GRAPHIC



## CONSPECTUS

20th- and 21st-century oil paintings are presenting a range of challenging conservation problems that can be distinctly different from those noted in paintings from previous centuries. These include the formation of vulnerable surface ‘skins’ of medium and exudates on paint surfaces, efflorescence, unpredictable water and solvent sensitivity and incidence of paint dripping which can occur within a few years after the paintings were completed.

Physicochemical studies of modern oil paints and paintings in recent years have identified a range of possible causal factors for the noted sensitivity of painting surfaces to water and protic solvents, including the formation of water-soluble inorganic salts and/or the accumulation of diacids at the paint surface, which are oxidation products of the oil binder. Other studies have investigated the relationship between water sensitivity and the degree of hydrolysis of the binder, the proportions of free fatty and dicarboxylic acids formed, as well as the relative content of free metal soaps. Thus far, data indicate that the qualitative and quantitative composition of the non-polymerised fractions of the oil binder cannot be solely or directly related to the solvent sensitivity of the paint film. Conclusions therefore indicate that the polymeric network, formed upon the curing of the oil plays a fundamental role; suggesting that water sensitivity – at least in some cases - may be related to the poor development, and/or polar nature of the formed polymeric network rather than the composition of the non-polymerised fractions.

Poorly developed polymeric networks, in combination with the migration of polar fractions i.e. dicarboxylic and hydroxylated fatty acids towards the paint surface, can be related to other degradation phenomena, including the separation and migration of the paint binder which can lead to the presence of observable skins of medium, as well as the more alarming phenomenon of liquefying or dripping oil paints. It is thus crucial to understand the molecular composition of these paints and their physicochemical behaviour to aid the further development of appropriate conservation and preservation strategies, as the risks currently associated with surface cleaning treatments and other conservation procedures can be unacceptably high.

This account reviews the relationships between the degradation phenomena associated with modern oil paintings and the chemical composition of the oil binder; and proposes a molecular model for the development of water sensitivity and other noted degradation phenomena. It is suggested that water sensitivity (and possibly other degradation phenomena) are consequences of processes that take place upon curing, and in particular to the rate of formation and decomposition of alkoxyl and peroxyl radicals. These reactions are strongly dependent on the type of oil present, ambient environmental conditions, and the chemical and physical nature of the pigments and additives present in the paint formulation. When the curing environment is oxidising, the chemistry of peroxyl radicals dominates the reaction pathways, and oxidative decomposition of the paint film overwhelms cross-linking reactions.

## INTRODUCTION

Cultural Heritage is a non-renewable resource whose preservation, restoration and enhancement are key to continuous cultural development. Modern painted art chronicles rapid changes within societies, reflecting technical, political and social developments in recent and current history. Access to modern and contemporary art for present and future generations is key to identity and a powerful driver for innovation; however collections are at risk due to unprecedented, and often unpredictable conservation challenges which largely reflect changes in materials and artistic practice. In the 18th and 19th centuries, industrialisation led to significant developments in the range of materials available for use by artists and transferred much of the materials-based knowledge away from artists to manufacturing. This is most commonly symbolised by the 1841 invention of the collapsible paint tube, which facilitated painting outside of the studio for the first time, contributing to the birth of Impressionism. During the 19th C, paint manufacturers developed new larger-scale technologies for making paint and both manufacturers' and artists experimented with paint formulations to achieve a range of visual effects. With homogeneity in rheology and drying time as key goals, artists' oil paint manufacturers included a range of materials, including dispersion agents, plasticizers, fillers, driers and surfactants to paint formulations to create stable paints, increase shelf life and transportability etc. Across the 20th and 21st centuries, toxic inorganic pigments have been substituted with benign - and often cheaper - organic colorants to address health and safety issues, to control cost and to comply with environmental legislation.

Amongst cultural heritage professionals there is a growing awareness of complex conservation issues affecting painted art produced from the 19th century till now, which are often significantly different from those presented by oil paintings from earlier centuries.

### *Degradation issues of modern oil paintings*

The pioneering work of J.J. Boon and his co-workers described how, in the course of curing and maturation of an oil paint film, polymerisation of polyunsaturated glycerides coexist with hydrolysis of ester bonds, formation of new oxygen-containing functional groups, oxidative cleavage of the fatty acid hydrocarbon chains, and metal ion co-ordination of the fatty acid group of the cross-linked material and non-cross-linked fractions[1,2]. All these reactions were shown to lead to the formation of paint film containing both mobile and stationary phases[1], which have been proven by numerous authors in the following years to be linked to the appearance and condition of a painting.

Phenomena regularly observed in modern oil paintings include the formation of vulnerable 'medium skins' on paint surfaces (Figure 1), fatty acid and metal soap efflorescence, water- and solvent-sensitivity, the formation of oil exudates on paint surfaces, delamination of paint layers, softened paints, and occasionally alarming incidences of dripping paints which have been known to occur within ten years after painting[3].

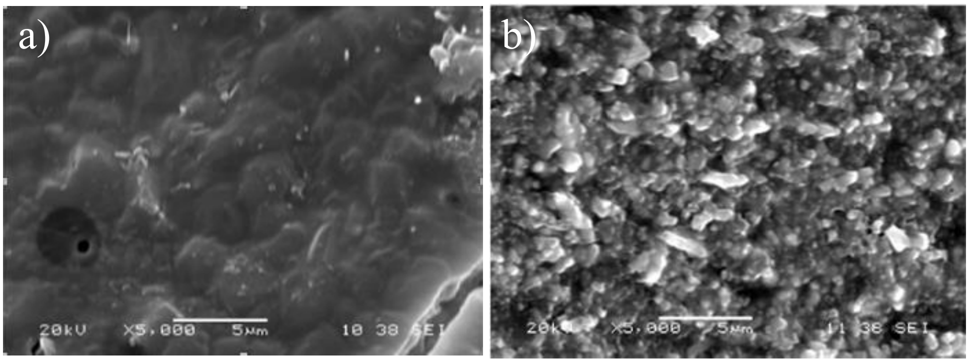


**Figure 1** Willem de Kooning (1904-1997), *Rosy-Fingered Dawn at Louse Point*, oil on canvas, 1963. Stedelijk Museum, Amsterdam. The surface of this painting is extremely sensitive to solvents and interaction of the solvent removes the degraded skin of medium, causing loss of surface gloss; a) Secondary electron image of a sample from the untreated white paint surface, showing medium-rich organic skin at surface coating the pigment particles beneath; b) Secondary electron image from a sample taken from the white paint surface after treatment with 0.5% ammonium citrate, pH6.5: the medium-rich organic skin has been removed, exposing the pigment particles that scatter light, creating a matt surface on visual inspection (Reproduced with permission from Tempest, unpublished dissertation Courtauld Institute of Art 2010).

Among the issues encountered, water sensitivity is proving particularly challenging, as the removal of accumulated, deposited soiling, often known as surface cleaning, traditionally relies upon water as the key component. In these cases, water may not be safely applied without causing undesirable surface disruption and pigment pick-up[3-7].

Water sensitivity has now been identified in model oil paint samples prepared from raw materials[4,8,9], in samples taken from batches of manufactured paint[10], and in several paintings [9-13]. Sensitivity may be limited to certain colours, may affect the whole surface of a painting, may be specific to some paint brands or lines, and may affect specific pigments across several brands [8,10,13].

Recent research has identified some of the causes and/or contributing factors relating to the changes observed in modern oils (i.e. water sensitivity and poor drying behaviour) including: the conversion of magnesium carbonate filler material used in some artists' paints to water-soluble magnesium sulphate heptahydrate salts at paint surfaces[4] (Figure 2), the migration of polar diacids to oil paint surfaces[6], and in some cases, the use of semi- or non-drying oils such as safflower [14,15] or palm oil[16] as the binder or proportion of the binder.

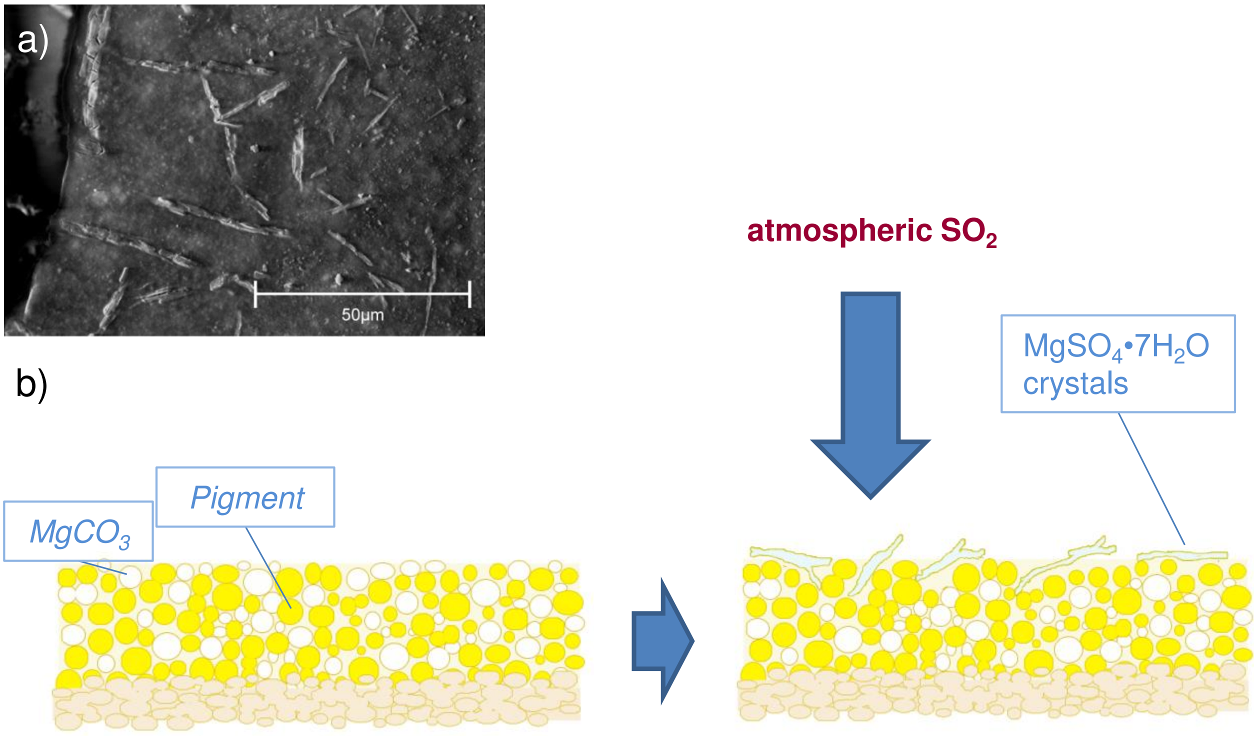


**Figure 2.** a) Secondary electron microscope image of water sensitive cobalt violet oil paint from Jasper Johns Untitled 1964-'65; Stedelijk Museum, Amsterdam: epsomite crystals are visible protruding through the surface. b) Schematic representation of influence of atmospheric $SO_2$ (levels peaked between 1950 - 1970) on paints containing $MgCO_3$, a common additive in modern paints (used as filler to reduce the amount of pigment, lowering costs). Adapted with permission from Silvester et all[4] Copyright (2014) Taylor and Francis.

Research carried out as part of the JPI Cultural Heritage funded Cleaning Modern Oil Paintings (CMOP) project[17] focussed on characterising water sensitive and non-water sensitive modern oil paint samples taken from over 50 paintings from the 20th century, and over 70 paint outs among paint swatches made by paint manufacturers as drying time tests, and model samples prepared using paints from several artists' paint manufacturers. One of the research questions within CMOP was formed from the observation that - especially when water sensitivity cannot be attributed to the presence of epsomite crystals – aqueous and ethanol extracts of sensitive paints are characterised by relatively high amounts of dicarboxylic acids[10], which are possible peroxide decomposition products formed upon the curing of a drying oil[18]. Moreover, it was shown that non-water sensitive paints (within the limitations of the paints studied) commonly presented a relatively low degree of oxidation as indicated by the total azelaic acid content, while water-sensitive paints presented varying degrees of oxidation[10,19].

As the group of diacids are inherently more water-soluble than monocarboxylic fatty acids (e.g. aqueous solubility at 20°C of azelaic acid: 0.01272 mols/L; palmitic acid 0.00003 mols/L), an hypothesis that water solubility may be related to increased diacid content resulting from a higher degree of oxidation and hydrolysis of the binding medium, was originally proposed at the beginning of the CMOP project. Similarly, when metal soaps are formed between the cations of certain pigments and driers (such as Zn, Pb, Cu), and acidic moieties present in the paint film (produced as a consequence of oxidation of unsaturated fatty acids, and/or hydrolysis of glycerides), a paint is less likely to be water sensitive. Fatty acid soaps of alkaline earth or heavy metals are highly insoluble,[20] and are believed therefore to contribute to the stability of the paint film by forming an ionomer-like network[21,22].

Model oil paint samples made with the same type of pigment and oil, the same pigment:medium ratio and aged under the same conditions, but containing different additives, were observed to develop varying degrees of water-sensitivity[23]. Interestingly, for this group of samples, the degree of water sensitivity did not appear to relate to the total content of dicarboxylic acids (i.e. free dicarboxylic acids, and those covalently bound to glycerides and metal coordinated to the ionomer like network, nor the free dicarboxylic acid content, nor the metal soap content of free (non-crosslinked) fatty and dicarboxylic acids, and to the overall degree of hydrolysis of ester bonds within the oil medium[24].

In a further study of two Winsor & Newton (W&N) artists' oil paint swatches where the paints contained the same pigment (phthalocyanine green, PG7), the same blends of oil (linseed and safflower) and had a closely similar inorganic composition were investigated. One of the swatches (dating to 2003) is now water sensitive, whilst the other (dating to 1993) is not. Water sensitivity appeared to be related to the degree of cross-linking and oxidation of the paint, where the water sensitive paint (2003) had a more polar and less extensively polymerized network[25]. Such difference in the degree of cross-linking might be related to the age difference between the two paints. This led to the hypothesis that poorly developed and polar polymeric networks are more likely to be affected by water and other polar solvents. During solvent cleaning, via diffusion and swelling mechanisms, the dissolution of non-polymerized diacids present both in the bulk film and on the paint surface may occur, resulting in observable pigment pick-up and surface change.

The insufficient formation of the polymeric network, as well as the migration of polar fractions comprised of dicarboxylic and hydroxylated fatty acids is also associated with other observed degradation phenomena, such as the migration and exudation of the paint binder[26](Figure 3, left), as well as the phenomenon of liquefying or dripping paints[14,15,27-30] (Figure 3, right).

**Figure 3.** Left: liquefying or dripping paint: detail from *Harvest* (1993) by Otto Piene. Reproduced with permission from Schulz [30] Copyright (2011) ICOM-CC. Centre: exudation of the oil binder on the paint surface visible as yellow protrusion in the white paint; detail from *Lover's Duet* (2008) by Ana Tzarev. Reproduced with permission from Bayliss at all [26] Copyright (2016) Elsevier. Right: cobalt blue dripping paint: detail from Composition (1952) by Jean-Paul Riopelle; Photo: Ida Antonia Tank Bronken. Reproduced with permission.

Paint exudates and drips have been shown to be generally characterised by a relatively high content of diacids and hydroxyacids at paint surfaces when compared to the bulk film. This has been attributed to the fact that although a cross-linked network may form upon curing, a fraction of triglycerides – possibly containing mono-unsaturated fatty acids, may fail to crosslink to the wider network and oxidise to form acidic and hydroxylated polar moieties. When these oxidised species cannot chemically bind with pigments, they are free to migrate to the paint surface, via a phase-separation mechanism leading to the formation of exudates, drips and tacky surfaces [14,15,26-29].

As a lack of polymerization and higher degrees of oxidation of the binder appear to be associated with several kinds of degradation phenomena in modern oil paints, the film curing process, which entails crosslinking and the oxidation of triglycerides of polyunsaturated fatty acids, is likely to be key in determining the establishment of these phenomena

## Paint curing

### *Oil fraction*

The curing of a drying oil is an autoxidative process. It is not a thermodynamically spontaneous process, as ground state triplet oxygen cannot directly add to the singlet state double bonds of unsaturated fatty acids[31]. Light and heat provide the high energy required to extract hydrogen atoms from unsaturated glycerides and form *ab initio* radicals (R·), and certain metals lower the energy barrier.  In the case of an oil paint layer the formation of R· may be catalysed by pigments often containing heavy metals and possibly driers, fillers and other additives, which can be additional sources of metal ions.

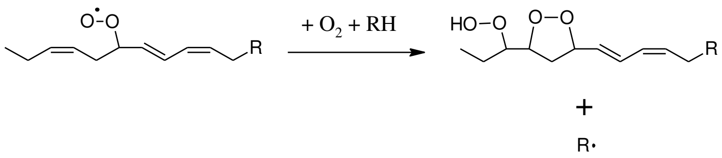
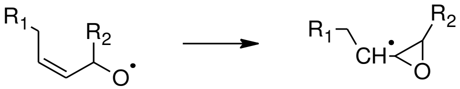
Once the radical R· is formed, under ambient oxygen pressure, oxygen can be added to form a peroxyl radical ROO·. According to classical theory for the autoxidation of lipids, once ROO· is formed, propagation begins, with ROO· abstracting hydrogens from nearby molecules to form a relatively stable intermediate hydroperoxide (ROOH) while generating a new radical (R’·) at the same time[32]. Hydroperoxides may decompose to alkoxyl radicals (RO·) and OH·. This step is considered to be the key rate-limiting step[33] based on the fact that it is the only propagation step involving any significant activation energy[34].

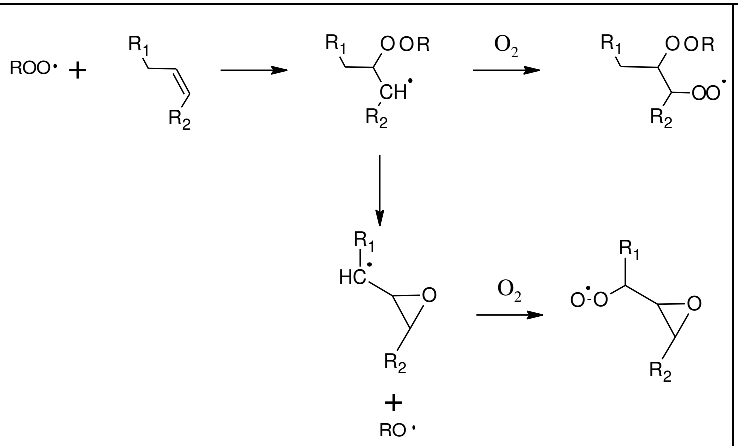
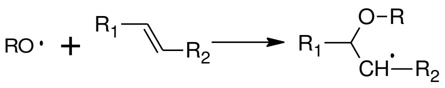
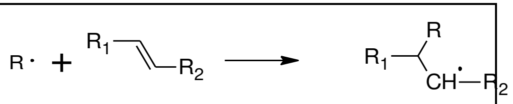
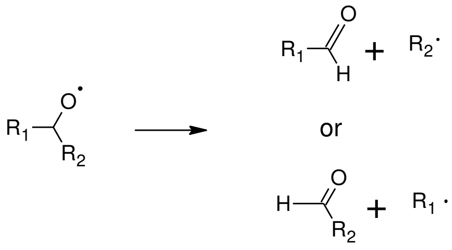
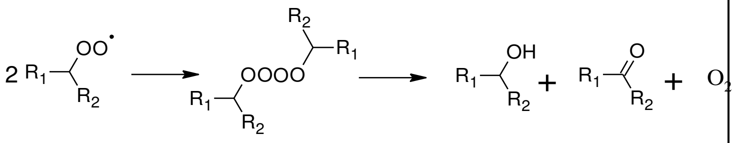
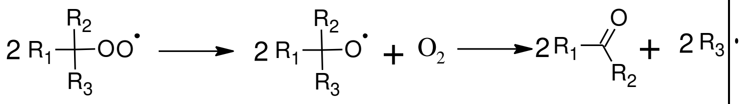
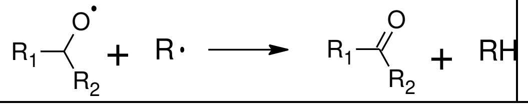
Termination reactions resulting from the recombination of radicals allow the formation of non-radical products, such as relatively unstable peroxides, or the relatively stable products of cross-linking reactions and oxidation [35]. When peroxides are formed, these will react further with time, undergoing scission and forming alcoxyl radicals (RO·). Some of the oxidation products are low molecular weight and may remain liquid inside the network, or slowly volatilise. Other oxidation products may further oxidise, ultimately leading to the formation of acidic moieties[36].

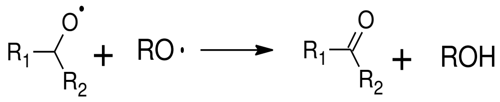
Cross-linking reactions result in the formation of oligomers, causing an increase in viscosity of the paint film, until a polymer network is formed, resulting in a rubbery solid paint film. In the earlier stages of curing, the polymer and oxidation products contain double bonds,[36] and it has been shown that the oligomers formed initially contain an intact number of double bonds[37]. Overall, the 'young' paint layer is relatively macromolecular and non-polar. Unreacted double bonds continue to react over time[38,39] and we hypothesise that at this stage, the reaction pathways leading to water-sensitivity and other degradation issues may become established.

The literature on oxidation of lipids, mostly focussed around food research, describes the complex reactions involved in the autoxidation of lipids[31,32,38-41]. The lipid oxidation kinetics and the observed reaction products are frequently inconsistent with expected reactions or product patterns, based on traditional free-radical chain reaction models[41]. It has been proposed that such discrepancies can be ascribed to the fact that both ROO· and RO· may undergo other alternative reaction pathways - in competition with hydrogen abstraction[41]. A summary of the main reactions that ROO· and RO· may undergo is shown in Table 1.

**Table 1.** Summary of the main reactions taking place upon lipid autoxidation [32,38,39,41].

| process | ROO· | RO· | R· |
|---|---|---|---|
| Initiation | | | $RH \rightarrow R\cdot$ |
| Addition of $O_2$ | | | $R\cdot + O_2 \rightarrow ROO\cdot$ |
| Hydrogen Abstraction | $ROO\cdot + RH \rightarrow ROOH + R\cdot$<br>$ROO\cdot + R_1OOH \rightarrow ROOH + R_1OO\cdot$ | $RO\cdot + RH \rightarrow ROH + R\cdot$<br>$RO\cdot + R_1OOH \rightarrow ROH + R_1OO\cdot$ | |
| β-Elimination of Oxygen | $ROO\cdot \rightarrow R\cdot + O_2$ | | |
| Internal rearrangement |  |  | |

| | | | |
|---|---|---|---|
| Addition to double bonds |  |  |  |
| (α and) β-scission | $ROO\cdot + R_1OO\cdot \rightarrow [ROOOOR_1] \rightarrow RO\cdot + \cdot OOR_1 \rightarrow RO\cdot + O_2 + \cdot OR_1$ |  | |
| Disproportionation | $ROO\cdot + R_1OO\cdot \rightarrow [ROOOOR_1] \rightarrow ROOR_1 + O_2$ | | |
| Recombination | <br> | $RO\cdot + R_1O\cdot \rightarrow ROOR_1$<br>$RO\cdot + R_1\cdot \rightarrow ROR_1$<br> | $R\cdot + R_1\cdot \rightarrow R\text{-}R_1$<br>$R\cdot + R_1O\cdot \rightarrow ROR_1$ |

|  |  |  |  |
|---|---|---|---|
|  | $2\ ROO\cdot \rightarrow [ROO\cdot\ O_2\ \cdot OR] \rightarrow 2RO\cdot + O_2$<br>or<br>$ROOO + O_2$ |  | $R\cdot + R_1OO\cdot \rightarrow ROOR_1$ |

ROO· may generate R·, RO·, other peroxides and hydroxyperoxides, as well as non-radical oxidation products such as epoxides and ketones. RO· may generate R· and non-radical oxidation products such as alcohols, aldehydes and ketones.

Cross-linking with the formation of a stable bond ($R_1OR_2$, $R_1R_2$) - which is fundamental to paint curing - occurs only when R· and RO· radicals add to double bonds and when R· and RO· radicals recombine (Scheme 1).

**Scheme 1.** Recombination reactions leading to the formation of stable cross-links

$R_1O\cdot + R_2\cdot \rightarrow R_1OR_2$

$R_1\cdot + R_2\cdot \rightarrow R_1R_2$

ROO· may also add to double bonds, resulting in peroxide crosslinks which will be subject to further reactions (Table 1). It is thus reasonable to suggest that one key factor that determines the formation of an extensive and relatively non-polar polymeric network may be the result of the differing chemistries of ROO· and RO·, whose rate of formation and decomposition depends on several influencing factors, including the paint thickness, the nature of the pigments and additives present in the paint formulation, the type of oil, and the curing environmental conditions.

*Pigments and additives*

It is reported that depending on the environment, the decomposition of ROOH may follow different pathways (Scheme 2) [32,42]

**Scheme 2.** Possible pathways of decomposition of ROOH [32,42]

ROOH → RO· + OH– (reducing metals)

ROOH → ROO· + H+ (oxidizing metals)

ROOH → RO· + ·OH (heat and UV, and through driers)

In the presence of ultraviolet (UV) light and/or through driers (that do not affect the oxidation/reduction process[42]), ROOH is quickly converted into RO· + ·OH. As a result, curing follows a reaction pathway ultimately leading to the formation of a stable paint containing oxidised species together with a well-established polymeric network (Table 1, Scheme 1). Lead white containing paints tend not to be water sensitive[10,43]. Lead based pigments are known to act as efficient through driers[44], which quickly lead to a full consumption of double bonds and the formation of dicarboxylic acids and a polymerised network. It has been proven that catalysis takes place when lead dissolves into the paint, and thus the kinetics and efficiency of the curing process depends on the pigment, the presence of impurities and residues of the pigment preparation process, and ambient environmental conditions[44]. Basic lead carbonate has been extensively used as white pigment in oil paints since antiquity, however it was largely substituted by other white pigments in the early-to-mid-20th century by manufacturers due to toxicity concerns[44]. As a result, formulations of modern artists' and industrial white oil paints are mostly devoid of lead and now contain titanium and/or zinc oxides.

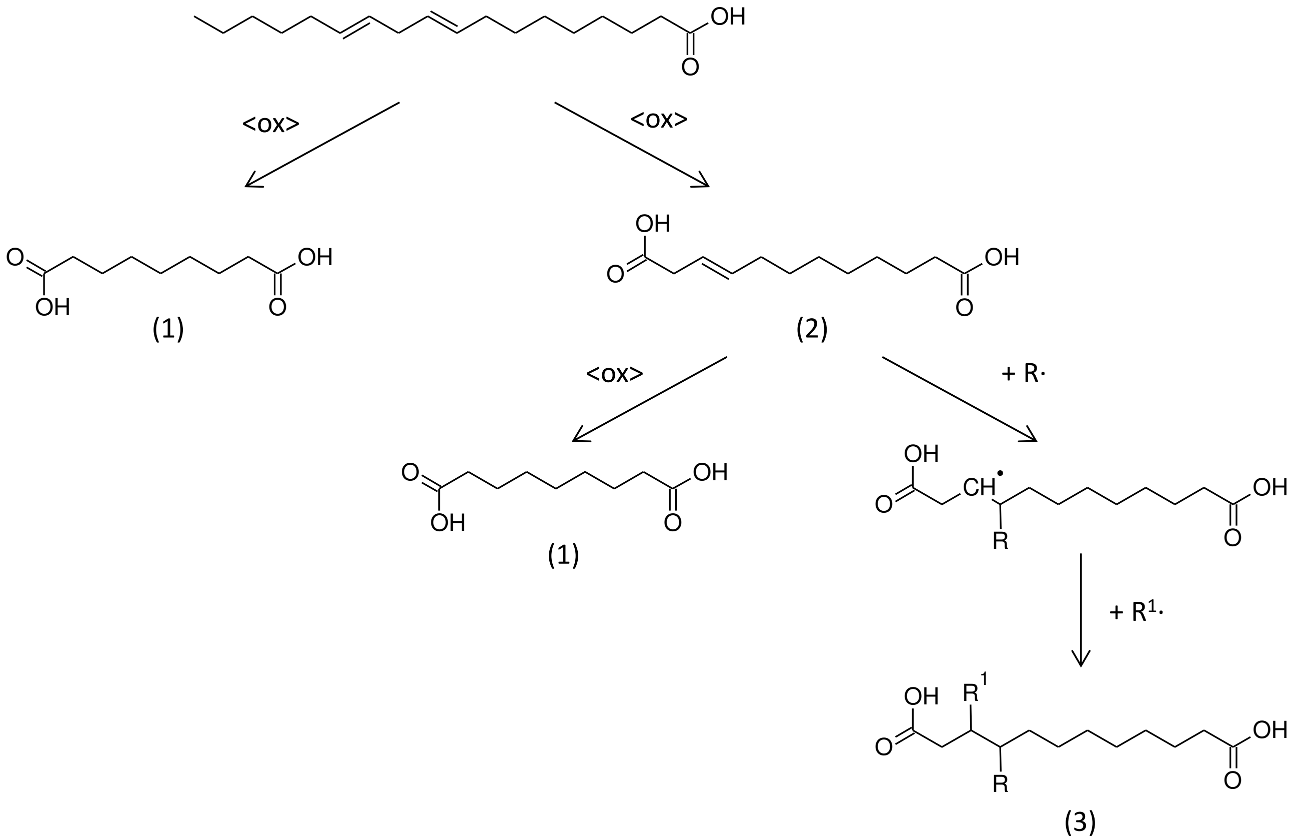
In an oxidative environment, curing is dominated by the reactivity of peroxyl radicals (Scheme 2). With reference to the reaction schemes shown in Table 1, ROO▪ results in more oxygen addition in comparison to RO▪ (see " internal rearrangement, addition to double bonds, and recombination reactions"), thus forming a paint film containing a relatively high proportion of oxidised compounds and a relatively lower proportion of cross-linked network.

On this basis, it may be hypothesised that in an oxidising environment after the initial stage of formation of oligomers and the cross-linked network, any remaining unreacted double bonds may be subject to oxidative degradation, predominantly following the reaction pathway of ROO▪ which leads to the fragmentation of the polymeric network and the formation of non-crosslinked, relatively low molecular weight polar species. Such a paint is likely to be vulnerable to the action of water via diffusion, facilitated by both an insufficient degree of crosslinking coupled with the relative hydrophilicity of the paint film, leading to swelling, solubilisation of polar compounds and a general vulnerability to mechanical action.

This hypothesis is consistent with observable characteristics of water sensitive paints such as: they may contain a higher content of extractable dicarboxylic acids and/or oxidised glycerides; they may contain higher amounts of hydroxylated and acidic moieties covalently bound to the polymeric network[10,25] derived from the formation of cross-linked dicarboxylic acids[24].

Dicarboxylic acids are end-products of the oxidation of drying oils[45] . When using established analytical methods based on chromatographic techniques, azelaic acid is the most abundant product of oxidation observed[45], deriving from the oxidation of unsaturated fatty acids with an unsaturation in position 9. In polyunsaturated fatty acids, oxidation may equally occur at other positions. In these cases, dicarboxylic acids are formed, which still contain double bonds in their structure. The unreacted double bond may undergo further oxidation or cross-linking and as a result, a dicarboxylic acid covalently bound to the polymeric network can be formed (Scheme 3).

**Scheme 3.** Possible pathways of oxidation of linoleic acid leading to the formation of azelaic acid (1) or dodec-3-enedioic acid (2). Dodec-3-enedioic acid (2) can further oxidise to azelaic acid (1) or undergo cross-linking. In the figure, cross-linking is depicted as a consequence of the addition of radical R▪ to the double bond of dodec-3-enedioic acid, followed by recombination with radical $R^1$▪. The final result is that dodecandioic acid is covalently cross-linked (3).



Another, undocumented but possible pathway of oxidation of the developing polymeric network may relate to oxidation at the alpha position to carbonyl groups of glycerides and acids. Although hydrogen abstraction in this position is less energetically favourable than in allylic positions, it requires less energy than in an internal alkane C-H: dissociation energy of allylic C-H: 350-370 kJ/mol, α to a carbonyl C-H: 390-400 kJ/mol, internal alkane C-H: 410-420 kJ/mol[46]. Furthermore, oxidation of methyl or methylene groups α to a carbonyl can be promoted in specific conditions to give hydroxyl ketones, aldehydes, or carboxylic acid derivatives[47]. These reactions require either certain enzymes or oxygen in combination with specific catalysts, including Mn-based compounds[47]. Hydrogen abstraction as well as hydroxylation α to a carbonyl might lead, upon further oxidation, to the formation of oxalic acid. Insoluble salts of oxalic acid, mostly Ca, Cu, and Zn, have extensively been observed in cultural artefacts, including paint layers[48-50], and their formation is commonly believed to be the result of the biological or chemical degradation of the organic binder[49,51,52].

Curing dominated by the reactivity of peroxyl radicals is likely for paint mixtures containing surface driers (or oxidative driers[42]), such as Co (II) soaps, or pigments and/or driers based on oxidising metals (such as Fe(III), Mn(IV), etc.). Actually, paints containing Earth pigments [Fe(III) and Mn(IV)], chromium green [(Cr(III)], cobalt blue [Co(II)] and ultramarine blue have frequently been reported as water sensitive[10].

Although Co (II) is not an oxidiser, driers based on Co (II)[37,42] are classified as primary driers or oxidative driers. Co-based driers promote the isomerisation of double bonds and the formation of conjugated systems[37]. The curing mechanisms of conjugated double bonds are different to those of fatty acids containing bis-allylic carbons. When conjugated double bonds are present, the addition of RO▪ and ROO▪ to double bonds is favoured[17]. Co-based driers are also capable of catalysing the decomposition of ROOH into RO▪ and ▪OH. In addition, it has been shown that Co (II) may react with oxygen at the paint-air interface to produce singlet oxygen, which is very reactive towards double bonds, forming cyclic peroxide structures and hydroperoxides. Hence the classification of Co (II) based driers (generally sold as Co soaps) as oxidative driers[42]. One experiment showed that, after catalysing the formation of oligomeric structures during curing of ethyl linoleate, in the long term a Co based drier promoted a series of decomposition reactions which overwhelmed the polymerisation reactions[37]. Similar phenomena may take place in paints containing Co-based pigments where, after an initial stage in which drying and subsequently polymerisation has taken place, other reaction pathways become dominant, leading to the oxidative degradation/fragmentation of the paint film[35,37].

Earth pigments [Fe(III) and Mn(IV)] are often associated with a very high level of oxidation[10,24]. In particular, in water-sensitive mature oil paint films containing iron-based pigments, the relative content of azelaic acid is quite high, as well as the relative content of dicarboxylic acids that are covalently bound to the polymeric network[10] (Scheme 3).

With regard to ultramarine blue paints, which are frequently associated with water sensitivity[10], recent studies have shown that with exposure to UV light, ultramarine blue pigment is capable of photo-catalysing the degradation of oil paints via a free radical process[53]. Ultramarine blue containing oil paints are slower to dry than lead white-based paints, and are characterised by relatively high levels of oxidation products, including oxidised di- and tri-glycerides and dicarboxylic acids[10]. Interestingly, ultramarine-containing paints are often associated with oxalate patinas in Italian paintings from the 15th and 16th centuries[54].

Water sensitivity is however, not unequivocally ascribable to paints containing a relatively high content of dicarboxylic acids, and/or oxidised di- and tri-glycerides. When metal soaps are formed as the product of reactions between fatty acids and certain cations, the metal might become an active catalyst, as has been established for lead white[44], manganese oxide, and certain other metals[55]. In these conditions, oxidative degradation of the polymeric network may take place, which may not necessarily lead to the formation of free dicarboxylic acids, and may not therefore be detected using standard chromatographic methods. In addition, pigments and additives containing reactive metals may also form carboxylates via reactions with acidic moieties produced by hydrolysis and/or oxidation of the drying oil. Studies indicate that metal soap interactions become an integral part of a cross-linked, ionomer-like network, in which acidic moieties are covalently bound to the polymeric network and free fatty- and dicarboxylic acids are coordinated with active metals within a three-dimensional structure[21,22,24,56,57]. The relative significance of metal soap interactions vs. covalent crosslinks for the stability of mature oil films is not yet fully understood. However, metal soap interactions are generally considered to contribute towards the stability of the paint film, given that metal soaps of alkaline earth and transition metals are all highly insoluble. Indeed, lead white and zinc white containing paints, which readily form metal soaps in oil, are almost never water sensitive[10]. Moreover, it was shown that paints that drip contain lower amounts of the pigments and extenders that allow the formation of metal-ionic bridges with the organic moieties, such as those containing lead, zinc, copper and even calcium[28]. It is reported that " lack of this anchoring stabilisation leads to accumulation of polar fractions and results in softening and eventually dripping of the paint" [28].

For many other pigments (such as those containing other metal ions not listed above and synthetic organic pigments) no general tendencies have been observed. In this case, the same pigment may or may not show water sensitivity irrespective of the paint brand and age[10], which could be due to the environmental conditions in which the paint films cure and age (see paragraph *External Environment*), as well as possible changes in paint formulation, as well as artist addition and amendments. In fact, the presence of additives, pigment particle size, underlying paint layers, trace ingredients and unreacted species remaining from formulation processes as well as the presence and type of any applied pigment coating may all contribute to the dominant reaction pathway(s) of the curing process[24,55,58].

### *Oil type*

Traditionally, drying oils such as linseed were used by artists, however modern oil paint formulations often contain a range of different drying and semi-drying oils [10,24], and in some cases, even non-drying oils[16]. The linolenic acid content of these oils varies considerably, which directly impacts upon drying properties. Linseed oil has a very high content of linolenic acid, whilst semi-drying oils, such as safflower, soybean and sunflower are mainly composed of glycerides of oleic and linoleic acids[59]. Linolenic acid contains three non-conjugated double bonds, and two bis-allylic carbon atoms. Linoleic acid contains two non-conjugated double bonds and one bis-allylic carbon, and oleic acid contains one double bond and no bis-allylic carbon atoms. The presence of double bonds, allylic and/or bis-allylic carbon atoms is directly related to the reactivity of these fatty acids, and hence the different oils, towards the formation of alcoxyl and peroxyl radicals.

RO· hydrogen abstraction is very fast[32], and less selective than ROO·, as RO· may abstract hydrogens both at the allylic and bis-allylic positions. Conversely, ROO· can only abstract bis-allylic hydrogens, and has a half-life several orders of magnitude longer than RO·[32]. In an oxidising environment, ROO· dominates the curing of the oil (Scheme 2), and in this case the limited number of bis-allylic positions of linoleic acid might favour the addition of ROO· to double bonds in preference to hydrogen abstraction[38] thus, favouring oxidative pathways. Furthermore, the availability of bis-allylic hydrogens may be further reduced by the increasing viscosity of the developing polymeric network, leading to an increased rate of alternative reaction pathways for ROO▪ radicals (Table 1) during advanced stages of curing. On this basis, it may be expected that a semi-drying oil may be more prone to the formation of a highly oxidised paint film, and thus more susceptible to water sensitivity.

### *External environment*

The environment in which the curing of an oil paint takes place is also likely to play an important role. High relative humidity in conjunction with sulphur dioxide exposure are known to favour the transformation of magnesium carbonate into soluble epsomite, a known cause of water sensitivity[4]. Water activity also strongly affects the rate and pathways of lipid oxidation[34] and it has been shown that the exposure of paints to high relative humidity may cause oxidation, both when the paint is young and also in paints cured over 10 years[60]. This may be due to the fact that high relative humidity enhances the mobilisation of catalysts and radicals[38]. If high relative humidity may favour oxidation, it is reasonable to hypothesise that curing at high relative humidity levels might favour the development of water sensitivity. This was supported by in a recent study, in which Winsor & Newton artists oil colour paints in three selected colours (French ultramarine, yellow ochre, cadmium yellow) were cured under ambient conditions for six weeks before being accelerated light aged at elevated relative humidity (70-80%), at 30°C, under an average of ~3500 lux illumination with the ultraviolet (UV) component filtered out. Samples became water-sensitive after 2.5 months under these conditions[61].

## Conclusions

Based on the authors previous research, and other studies presented in the literature, this paper presents the hypothesis that water sensitivity as well as other degradation phenomena of modern oil paintings are related to a lack of polymerization and excess oxidation of the oil binder. As these reactions relate to the oil curing, the paper investigates chemical reactions known to be involved in the oxidation of lipids. Experimental evidence presented in previous research, together with a careful review of reactions involved in the oxidation of lipids leads to the hypothesis that a lack of polymerisation and high degree of oxidation can be linked with different reaction pathways that involve the evolution of peroxyl and alkoxyl radicals formed upon curing. We conclude that when the chemistry of peroxyl radicals dominates the reaction pathways, oxidative decomposition of the paint film overwhelms cross-linking reactions. We show that; i) the type of oil - and in particular the use of semi-drying oils; ii) the use of oxidising pigments; iii) the lack of use of through driers - lead pigments largely used in the past have been disappearing form modern oil paint formulations for health reasons; iv) the environmental conditions in which the paint cures; can all contribute to the formation of an excess of peroxyl radicals, ultimately leading to a failure in forming an extensive and relatively non-polar cross-linked network in favour of extensive oxidation.

Many complexities are involved in this type of research, and several aspects warrant further investigation. Paintings are in fact significantly more complex than model paints, being multilayered and often blended systems. The nature, porosity and water affinity of paint underlayers, the presence/absence of a protective layer of varnish; the presence/absence of a paint frame, the nature of each paint layer, the use of synthetic organic pigments and the lack of metals capable of anchoring the formed cross-linked network and polar mobile phases, as well as the conservation history, all contribute to determining the molecular composition of a painting, and thus its appearance and condition. Multi-analytical approaches for the study of model paints must thus be associated with investigations of works of art.

From the methodological point of view, one of the biggest challenges relates to advancing scientific methods for the detailed molecular characterisation of the insoluble polymerised fraction of the oil, which still remains difficult/impossible for most molecular techniques. Nuclear magnetic resonance based techniques together to computational approaches may potentially offer information about the effects of water and other hydrogen containing moieties in a larger data set that would be a useful contribution to studies in this context.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. ‡These authors contributed equally. (match statement to author names with a symbol)

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