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A molecular perspective on the cleaning of oil paintings

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CHAPTER

EIGHT

A REVIEW OF SOLVENT ACTION IN OIL PAINT

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8.1 Introduction

The French philosopher Étienne Gilson once said: 'There are two ways for a painting to perish, the one is for it to be restored; the other is for it not to be restored.'¹⁹⁵ In order to resolve this dilemma, a paintings conservator ideally knows as much as possible about how the paint material can be adversely affected by cleaning.

The growing corpus of scientific literature dealing with the physicochemical aspects of oil paint alterations has shed new light on the possible unwanted side-effects of solvent-based cleaning.^{16,28,30,31,161} *In this review, we will discuss the known physicochemical processes that can be induced or enhanced by solvent exposure, and how these processes may be influenced by the properties of the paint material.*

Although conservators and conservation scientists now universally recognise that the majority of paintings is affected by diverse and widespread alteration phenomena, these phenomena remain poorly understood. As a result, paintings conservators routinely treat objects without a full understanding of the chemical processes and material properties of the paint. Examples of important paint alteration phenomena include cracking of the paint, the discoloration of pigments, the yellowing of varnishes, dirt accumulation, the formation of protrusions and crystalline material deposits on the surface and increased transparency of paint layers.^{1,3} The observation of these slow chemical alterations has resulted in the realisation that paintings can no longer be seen as static objects. For example, factors such as relative humidity (RH),^{99,100} solvent exposure,^{68,148,170} fluctuations in temperature¹⁷⁷ and exposure to light^{101,178,196,197} have been shown to enhance the alteration and degradation of oil paints. Many of these oil paint alteration processes are the result of pigment-binder reactions that lead to a change in the chemical structure of oil paintings, which can affect the stability and appearance of whole works of art. Solvent-swelling in particular can enhance the mobility of reactive paint components, which poses the risk of accelerating certain degradation phenomena.¹⁴⁸ However, although a considerable amount of progress has been made,^{16,31,174–176} the knowledge of the influence of solvent-based cleaning on fundamental chemical and physical processes does not currently allow for a reliable *estimation of the risks* involved in cleaning, which led to the consensus that solvent exposure on paintings should be minimised.

In order to assess the risks associated with solvent exposure, one should have extensive knowledge of the chemical and physical processes occurring in paint layers and know how these processes can be influenced by solvent exposure. Because most paintings necessarily undergo cleaning treatments, it is of vital importance for the conservation of works of art to advance our understanding of solvent action on oil paint and work towards a reliable assessment of the risks involved in solvent-based cleaning.

8.2 Physicochemical processes relevant for cleaning

For an accurate and complete description of the processes involved in solvent cleaning the following processes need to be considered: varnish dissolution, solvent swelling, –diffusion, –evaporation, –leaching and chemical reactions (see Figure 8.1a). In this review, we define the total combined physicochemical influence of these processes (Figure 8.1a) as *solvent action*. Therefore, solvent action can be viewed as a collective term describing the rate of solvent transport processes inside the paint, including chemical reactivity induced by the uptake of solvents. *Solubility* is well described by equilibrium thermodynamics (see Section 8.5.1). *Swelling* of paint, the only tangible phenomenon for a conservator, has two distinct aspects: equilibrium swelling and swelling kinetics. *Equilibrium swelling* is partly governed by thermodynamics, but needs additional parameters concerning polymer properties. *Swelling kinetics* involves mass (e.g. solvent) transport in the paint film, which places this process in the well-developed and vast scientific area of diffusion of low-molecular weight substances in polymers. Equilibrium and kinetic effects require a separate theoretical description, but the distinction between the two is often overlooked in art cleaning studies. A higher degree of complexity is faced when also considering *evaporation* of solvent in relation to its *retention time* in a paint film. Simultaneous description of evaporation and retention is a complex interplay of processes, since the rate of swelling and de-swelling may be limited by the rates of either evaporation from the surface or diffusion inside the film. Similarly complex processes are encountered in *leaching*, where diffusion of soluble extractables (non-crosslinked oxidation products) and solvent occur in opposite directions. Both transport processes may be rate-determining. The simultaneous transport of multiple species inside polymers is called multicomponent diffusion. The ultimate complexity occurs when all aforementioned processes occur together with *chemical reactions* invoked by reactive groups present in partially degraded paint films. Solvent-induced reactivity in paints has only recently been identified as a crucial and potentially artworks endangering issue.¹⁴⁸

All the aforementioned processes deserve a separate theoretical description, which defines the textual structure of this review paper: in order of increasing complexity. Nevertheless, it should be emphasised that in cleaning practice the different processes occur *simultaneously* (see Figure 8.1a). The extent to which either one of these processes occurs, depends on the amount of solvent that is applied (varying with application method) and the rate of solvent transport inside the paint. The rate of solvent transport inside the paint depends on the condition of the paint and is influenced by factors such as the presence of (micro) cracks or soluble extractable materials. It should also be recognised that these transport processes are generally interconnected. For example, faster diffusion will result in faster swelling¹²² and possibly in faster leaching and evaporation. Solvent-induced chemical reactions, such as zinc soap formation (discussed in Section 8.8), are happening at the same time as dissolution, diffusion and evaporation. For the conservator,

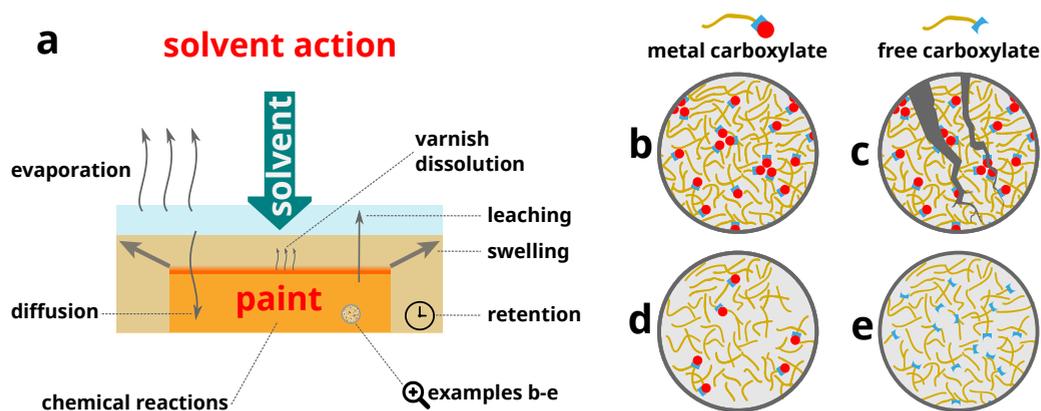


Figure 8.1 a: Physicochemical processes that occur simultaneously during cleaning operations, altogether defined as *solvent action*. b–d: schematic examples of possible structure in the polymeric binding medium in oil paint. b: aged ionomeric binding medium with metal carboxylates and high degree of cross-linking, c: cracked ionomeric binding medium with metal carboxylates and high degree of cross-linking (shown crack diameters are not to scale), d: ionomeric binding medium with metal carboxylates and low degree of cross-linking, e: highly oxidised binding medium with intermediate degree of cross-linking and a high concentration of free carboxylic acid groups.

the swelling of paint (possibly resulting in softening of the paint and pigment pickup) is the only tangible phenomenon in the list of processes mentioned above (Figure 8.1a). Although the change of gloss is sometimes attributed to leaching, it may also be due to re-deposition of varnish residues after cleaning or due to the increased visibility of the porosity of the paint that leads to blanching.¹⁹⁸ Because the diffusion of water in intact oil paints is very slow¹²² and the solubility of most paint components in water low, solvent diffusion –swelling and –leaching apply to a much lesser extent to aqueous cleaning.

The fact that no (analytical) techniques exist that can measure solvent action (Figure 8.1a) under realistic treatment conditions has seriously hampered quantitative studies on the influence of cleaning on oil paints. Moreover, some concessions generally need to be made by conservation scientists in the design of simulated cleaning treatment experiments. For example, an important factor in cleaning research is the choice between using model systems and real paintings for experiments. This decision may depend on the analytical methods and sample size, among other things, and is intimately related to the challenge of balancing the theoretical relevance (*e.g.* reproducibility) of the cleaning experiment and the practical relevance of the cleaning treatment. For example, the use of long immersion times for leaching studies may yield highly accurate data on extractables, but the results may be less easily translated into conservation strategies because of the short contact times encountered in cleaning practice. Finding the optimal balance between theoretical and practical relevance of cleaning experiments has led to many discussions.^{25–27,199} We will highlight the practical relevance of the literature discussed throughout this review.

8.3 A chemical view on oil paint

Solvent action (Figure 8.1a) depends strongly on the chemical and physical properties of the materials that will be exposed to solvents. To understand the origins of these material properties, a chemical view on oil paint can be taken. A chemical view on traditional and modern oil paint regards the paint material as a mixture of complex metal oxides or conjugated organic dyes (inorganic or organic pigments), a polymerised, triglyceride-based drying oil, and often a variety of additives. A painting is thus a metastable, multilayered, heterogeneous polymeric material. The material composition, stratigraphy of the paint layers with their respective chemical differences and state of degradation, constitute this complex polymeric material. Although a painting can be considered metastable as a whole, certain layers may *locally* respond differently to solvent exposure than others, resulting in disturbance of local chemical equilibrium due to the displacement or removal of non-crosslinked oil components. Consequently, understanding autoxidation of the oil,⁴⁻⁶ the degradation of pigments^{101,178,196,197,200}, pigment–binder interactions,⁸ the chemistry of varnishes^{16,20} and their degradation^{17-19,21} and the composition of dirt^{22,23} are a prerequisite to understand the influence of solvent action. All these factors are relevant when choosing the method to treat a paint surface, which depends on the chemical composition of the materials and their respective state of degradation.

8.3.1 Oil paint cleaning is polymer chemistry

Despite the overwhelming complexity of both paint materials and degradation phenomena, solvent action always concerns the transport and interaction of solvents within the polymeric binding medium. Therefore, in order to understand the influence of cleaning on oil paint, it is crucial to view oil paints as pigment-filled polymers and focus on the properties of the polymeric structure of the binding medium (Figure 8.1b–d). Because solvents diffuse and interact with these polymers, polymer properties such as degree of cross-linking, polarity, concentration of plasticisers and ion-content determine the sensitivity towards solvents. If the properties of the polymer change, the sensitivity for solvents changes. The properties of these drying oil-based polymers are determined by the chemical composition and the environmental conditions during the lifetime of a painting. The wide range of paint materials and environmental conditions results in diverse polymeric structures (see Figure 8.1b–d for examples), which determine to what extent solvent action (Figure 8.1a) can occur during cleaning treatments.

The polymer chemistry literature provides an abundance of relevant information for cleaning studies. An important example is that oil paint binding media in paintings where zinc or lead-based pigments are present, feature strong similarities with a class of metal-ion-containing polymers called *ionomers*.^{43,109} Ionomers were recently identified as representative models for mature oil paint binding media.^{43,109} However, they have been

widely studied for applications in packaging, adhesives, fuel cell membranes^{201,202}, biomimetic sensors,^{203,204} water purification²⁰⁵ and drug delivery.²⁰⁶ The network structure in oil paint ionomers is more complex than in most industrial ionomers due to the complexity of the triglyceride monomer itself and the complex autoxidation pathways responsible for network formation. Nevertheless, the available literature concerning transport of water and organic solvents in (ion-containing) polymers and alkyd resins^{44,55,60,61,207–209} provides a useful starting point for oil paint cleaning studies. Relevant examples include methodologies for measuring or modelling dynamic processes in polymers, such as solvent swelling and (multicomponent) diffusion, ion-transport^{46–52,103} and plasticiser-effects (such as added fatty acids or metal soap complexes^{155,210,211}). Vice versa, oil paint research can also stimulate and advance the use of uncommon analytical techniques such as two-dimensional infrared (2D-IR) spectroscopy¹⁰⁹ or In-Air Plasma-Induced Luminescence (In-Air-PIL) spectroscopy in material science.²¹² Considering the recently renewed interest in bio-based alkyd paints,^{213,214} efforts towards understanding oil paint chemistry are certainly relevant in the broader perspective of industrial applications and polymer science. Currently, the collaboration between polymer science and cleaning studies remains limited, but research initiatives that contribute to bridging this gap were recently presented.²⁹ In this review, several examples of how polymer research can advance the understanding of solvent transport in oil paint are given (see for example sections 8.5.2, 8.8 and 8.9).

8.3.2 Polymer structure and solvent sensitivity

In conservation science, the wide range of properties of the polymeric binding medium is not always recognised. Instead, polymer structure is often discussed in terms of differences in *solvent sensitivity*. Solvent sensitivity occurs in cases where the binding medium has such a low degree of polymerisation and high degree of oxidation (due to network degradation or inherently low cross-linking) that minor mechanical action removes pigment particles.¹¹ When water sensitivity is reported, high concentrations of extractable free dicarboxylic acids are often found,^{12–14} together with a low degree of polymerisation of the binding medium.¹⁵ Therefore, the wide variety of cases where solvents sensitivity is reported provide examples of how differences in the polymer properties of the binding medium influence solvent action. Because the majority of inorganic pigments are inert towards solvents or water, inorganic pigment properties generally only play an indirect role in solvent sensitivity due to their respective influence on the drying and ageing of the oil, resulting in differences in the polymeric structure of the binding medium. Besides the indirect influence of pigment chemical properties, the concentration of pigments also plays an important role in determining the final polymeric structure of the oil and therefore solvent sensitivity.

To discuss how chemical pigment properties and pigment concentration can influence the polymeric structure of the oil, a concept that originates from coatings literature named

critical pigment volume concentration (CPVC) is recommended. CPVC is defined as the 'random tightest possible packing of pigment particles and the minimum amount of binder necessary to fill the interstices between particles'.²¹⁵ Although the concept of CPVC is often used in the conservation field to define a workable paint with good coverage, it is often overlooked that pigment concentration strongly influences the curing of the paint due to the influence of PVC on oxygen diffusion. As a result, the polymer properties of the binding medium are influenced by the PVC, which in turn will influence how solvents will interact with the polymerised oil medium. It is known that many coating properties change significantly at the CPVC.²¹⁵ Below the CPVC the coating film is continuous and made only of binder and pigments. Above the CPVC the film is discontinuous due to the presence of air pockets around pigment particles that replace the binder.²¹⁵ The curing of alkyd paints (which crosslink via a similar mechanism as oil paint) depends on the PVC: below the CPVC the drying rate is independent of degree of pigmentation and a reaction front due to oxygen diffusion is observed, directed from the top of the paint inwards. Above the CPVC, a coating cures more homogeneously due to the faster oxygen diffusion through voids between pigment particles.²¹⁶

It is widely recognised that metal ions released by inorganic pigments can influence the drying of oils,^{5,6} which leads to vastly different properties in the resulting polymerised oil network. Examples of how pigment properties may influence the polymerisation of the binding medium, are paints based on ultramarine⁹ or anatase titanium dioxide¹⁰ pigments, which are known to enhance the breakdown of the binding medium and lead to the formation of powdery paints. Powdery paints can be considered to possess a $PVC > CPVC$, because only a small amount of binding medium remains intact. Notorious water sensitive paints include ultramarine blue^{9,31,217}, cobalt blue¹³ and cadmium and chrome yellow.¹² Certain synthetic organic pigments also have some inherent solubility in organic solvents,²¹⁸ which is probably the only scenario where the structure of the polymeric binding medium is less important and solvent sensitivity will be mostly determined by the properties of the solvent.

In general, paints containing organic pigments are more sensitive to organic solvents,²¹⁹ even though they often contain a $PVC < CPVC$. An interesting case illustrating how PVC and pigment properties may influence the polymerisation of the oil and result in solvent sensitivity, are medium-rich organic blacks. Firstly, inhomogeneous and incomplete drying limited by oxygen diffusion (due to the low PVC) may result in a low degree of cross-linking and explain how carbon or bone black paints are solvent sensitive. Secondly, the absence of metal ions causes organic blacks to lack metal carboxylate crosslinks. Thirdly, the absence of metal ions can influence the autoxidation of the binding medium, further reducing the degree of polymerisation and enhancing their solvent-sensitivity. Although it is currently unclear which of these hypotheses is most relevant, it is clear that the structure of the polymerised binding medium governs the degree of solvent sensitivity.

In summary, solvent sensitivity is intimately linked to the polymer properties of the

binding medium, which is indirectly affected by pigment type and concentration because these factors can influence the cross-linking of the oil.

8.4 Historical cleaning research

Scientists have been studying the effects of cleaning on paintings for more than two hundred years. The importance of the chemistry of paint and varnishes was even recognised in the 18th century. Trained as an apothecary, Robert Dossie (1717–1777) provided detailed information about cleaning practice for painted surfaces in his *Handmaid to the Arts* (1758).²²⁰ He noted that: ‘the art of cleaning pictures and paintings is of great consequence in preserving valuable works of that kind, but has been very little understood even by those who profess to practice it’.²²⁰ In the 19th century, a number of important scientists were involved in studies of paint chemistry.²²¹ In the 1850s, Michael Faraday (1791–1867) investigated varnishes, cleaning methods and the impact of coal smoke and gas lighting on the discoloration of surface coatings for the National Gallery in London. In the 1870s, the chemist and biologist, Louis Pasteur (1822–1895) investigated the yellowing of varnishes at the *Ecole des Beaux-Arts* in Paris.¹⁶ In Germany, Max von Pettenkofer (1818–1901), a Bavarian chemist, patented a process of exposing blanched paintings to alcohol vapour and copaiba balsam.¹⁶ The Pettenkofer method was later found to have induced ‘severe disruptions’ of the paint and varnish layers and paintings were sometimes referred to as being ‘Pettenkofered’, highlighting the risks involved in cleaning paintings.¹⁶ The role of chemists in conservation grew considerably in the 20th century when a scientific department was established at the *Staatliche Museen* in Berlin in 1888 and the British Museum in 1921.²²¹ Professor of chemistry Sir Arthur H. Church published his comprehensive handbook ‘*The Chemistry of Paints and Paintings*’ in 1915.²²² In the Netherlands, Martinus de Wild was probably the first to combine conservation and restoration with scientific training. In his dissertation (1928), de Wild provided an in-depth discussion on the chemistry of common traditional pigments and advice on the cleaning of paintings. For example, de Wild stated that it is ‘best to completely remove an old varnish layer’, that alcohol is an effective solvent for that purpose and that mixtures of solvents (*e.g.* alcohol and xylene) can be used to ‘decrease the rapid action of the alcohol’ if required.²²³

Systematic scientific studies focusing on solvent action on oil paint films took a leap in the 1950s. The early cleaning studies by Stolow^{53,93,224} have provided valuable insights for paintings conservation practice and are still a major source for the evaluation of solvent action on oil paint today. However, the effects of cleaning on paintings have also continually been a topic of considerable controversy.^{168,199,225} Besides the scarcity of technical literature, cultural and ethical aspects of cleaning make this a topic that is among ‘the most contentious’ of all the interventions works of art may undergo.²²⁵

8.5 Solubility, swelling and diffusion

The solubility of (aged) varnishes, oil components and unwanted polymeric materials in organic solvents is an important topic in cleaning studies because it determines how easily these materials can be removed. Before starting actual cleaning, solubility tests are often conducted on small areas of the painting to assess the solubility of the materials and choose a proper solvent (mixture) and method of application. It would however be desirable to predict the solubility of these materials using a theoretical model because this would enable an easier selection of cleaning tools and limit the risks associated with solubility tests. Hence, it is not surprising that some theoretical solubility models were developed or adapted from other fields of study.

8.5.1 Theoretical prediction of solubility

The Hildebrand and Hansen models

Solubility studies in art cleaning are mostly based on thermodynamics of dilute solutions. Thermodynamics of dilute solutions describe the equilibrium condition in solvent-solute (in our case mostly solvent-varnish) mixtures and therefore consider small amounts of solid materials to be dissolved and removed by cleaning solvents. However, the use of organic solvents on a painting hardly qualifies as a dilute solution, since a limited amount of solvent is used, the contact times are often short (which means solvent-solute equilibrium and equilibrium swelling may not be reached) and soluble paint components are encapsulated in a tightly crosslinked polymeric binding medium. Moreover, thermodynamics of dilute solutions do not account for energetic terms involved in the interaction of a solvent with the polymeric binding medium, which is often called non-ideal behaviour. Thermodynamic theories describes solvent-solute equilibrium in terms of ideal mixing behaviour and deviations thereof. In the Flory-Huggins (FH) theory²²⁶ such deviations are attributed to intermolecular interactions, expressed in terms of differences in molar volume and the FH interaction parameter. The use of FH theory to describe solubility is recommended and the interaction parameter is also used in the Flory-Rehner theory of polymer swelling, which is discussed in Section 8.5.2. Currently, only very few examples of FH theory are presented for cleaning science.²²⁷

In the 1950s, Hildebrand²²⁸ also formulated a theory describing non-ideal solvent-solute behaviour, which is related to the FH interaction parameter. Hildebrand's approach formed the basis for the most widespread model aiming to predict varnish solubility and minimise paint swelling used by the conservation community.²²⁹ The model is based on the Hildebrand total solubility parameter δ_t ,²²⁸ which is defined as the square root of the cohesive energy density, a measure of the intermolecular interactions within a pure solvent. The solubility parameter δ_t is related to the heat of mixing of the two components (solvent and solute) and approaches a minimum if the Hildebrand solubility parameters

of the solute and the solvent are close.²³⁰ To account for interactions between more polar molecules and for hydrogen bonding, Hansen subsequently developed a model with three parameters,^{231,232} later referred to as Hansen solubility parameters (HSP):

- δ_d dispersion forces
- δ_p dipolar intermolecular forces
- δ_h hydrogen bonds.

The HSPs add up to the Hildebrand total solubility parameter (δ_t) according to $\delta_t = \delta_d + \delta_p + \delta_h$ and can be treated as coordinates for a point in three dimensional space. The nearer two compounds are, the more likely they are to dissolve (often referred to as like-dissolves-like rule). To determine whether the parameters of two substances (usually a solvent and a polymer) are close, a value called interaction radius is given to the substance being dissolved. This value determines the radius of a sphere in Hansen space with the center defined by the HSPs. The HSPs formed the basis for the so called Teas chart,²²⁹ which is still used in cleaning science.

The Teas chart

In the Teas chart all three Hansen parameters are plotted on a single planar graph (see Figure 8.2). Teas parameters are fractions and are related to Hansen parameters through Equation 8.1. Hence, Teas parameters express the relative contribution (multiplied by 100 to obtain a percentage) of each Hansen parameter to the total Hildebrand value:

$$f_d = \frac{\delta_d}{\delta_d + \delta_p + \delta_h}, f_p = \frac{\delta_p}{\delta_d + \delta_p + \delta_h}, f_h = \frac{\delta_h}{\delta_d + \delta_p + \delta_h} \quad (8.1)$$

The construction of the Teas chart is based on the assumption that all materials have the same Hildebrand total solubility value (δ_t). According to this assumption, solubility behaviour is determined by the relative magnitude of the three molecular forces (δ_d , δ_p , δ_h) that contribute to the total Hildebrand value δ_t . However, since δ_t is not even approximately constant for different polymers,²³³ this approach leads to the loss of δ_t as independent parameter. For varnishes and drying-oil based polymers as the solute species, this seems to be a bad assumption and can lead to significant inaccuracy in the fractional Teas parameters.^{233,234} It should be emphasised that projecting three HSPs onto a triangular chart inevitably leads to the loss of information. As early as 1989, Stavroudis²³⁸ warned the conservation field about the severe limitations of the Teas chart (the titles were 'No Teas-ing' and 'Teas-Busters') and proposed to ban it. It was realised that, using the triangular Teas chart, the 'range of solubilities of a polymer is distorted' and 'relations between solvents are lost'.²³⁸ This issue was also put forward by Phenix, noting that

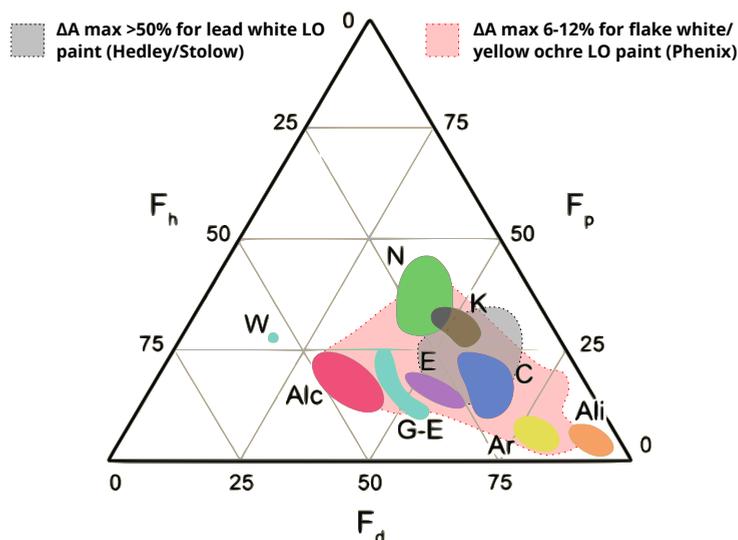


Figure 8.2 The Teas chart, projecting three dimensional Hansen solubility parameters onto a triangular space. 'Peak swelling' region identified by Hedley²³⁵ based on data from Stolow (see Section 8.5.2) in grey, extended 'peak swelling' region based on different paint types identified by Phenix in light red. W=water, N=nitrogen containing solvents, K=ketones, Alc=alcohols, G-E=glycol ethers and esters, E=esters, C=chlorinated solvents, Ar=aromatics, Ali=aliphatics. Image adapted from Chelazzi *et al.*²³⁶ and Phenix²³⁷.

solvents with clearly different solubility properties are clustered close together in the chart²³⁷ (see for example ketones and nitrogen containing solvents in Figure 8.2). In the Teas chart, most solvents fall within a narrow region of solubility parameters.

Other classification models

The relative inaccuracy of both Hildebrand and Hansen-based models (which includes the Teas chart) was recently illustrated in the review by Brouwer & Schuur. The prediction of activity coefficients at infinite dilution (γ_i^∞ , often used to characterise solvent-solute interactions) was compared for a range of models.²²⁶ The Hildebrand parameter features the largest error with an average relative deviation (ARD) of $>10^5\%$ in the γ_i^∞ prediction. Using the HSP to calculate the γ_i^∞ with significant improvement, compared to the Hildebrand model but still, an ARD of $66.4\% \pm 14.4\%$ is observed for solvents.²²⁶ More recently, models like COSMO-RS, the Abraham model and MOSCED have been developed that perform much better.²²⁶ The use of these models to predict solvent interactions with a range of materials used in conservation and restoration is recommended.

Phenix and Graczyk recently proposed the use of solvatochromic polarity as an indicator of solvent properties.^{84,162} This methods ranks solvents according to normalised Reichardt solvatochromic polarity (E_T^N) and refractive index (n). E_T^N values are polarity

values based on the colour changes of pyridinium-N-phenoxide betaine in a solvent and are referenced to the polarity of tetramethylsilane (TMS, apolar) and water (polar).²³⁹ The advantages of this model are that it provides an empirical description of the polarity of solvents and that E_T^N and n can readily be determined for unknown solvents or solvent mixtures. Concerning mixtures of solvents, significant deviations from linearity are observed in the relationship between E_T^N and n .¹⁶² Although plotting E_T^N versus n does show increased clustering within classes of solvents¹⁶² as compared to Teas or Hansen solubility parameters, the classifications of a wider range of solvents remains challenging.

In an attempt to do justice to the short contact times encountered in cleaning practice, a method that claims to take the dissolution rate of varnishes into account was developed by Zumbühl.⁸³ The dissolution rate of a range of varnishes was studied and found to strongly accelerate at vapour pressures exceeding 100 hPa (25 °C). The correlation between rate of dissolution and vapour pressure was also confirmed for the leaching of paints materials at short immersion times. Most importantly, it was found that the rate of dissolution after short solvent exposure is not influenced by the potential swelling capacity at longer timescales.⁸³ This study illustrates well the confusion that is created when attempting to explain kinetics (of dissolution) from purely thermodynamic equilibrium considerations (vapour pressure).

8.5.2 Swelling of paint by solvents

Solvent swelling is a tangible phenomenon because the mechanical and optical properties of the paint surface can change due to the swelling process. During the removal of old varnishes, swelling will result in an altered 'feel' of physical interaction with the paint surface during swabbing. Because of the expansion of the oil matrix by solvent ingress, swelling may result in pigment loss,¹² which prompts the conservator to change solvent, application method or halt the cleaning action.

Theoretical prediction of swelling

Most early literature on the cleaning of oil paint focused on the swelling- and de-swelling behaviour of relatively young oil paints films in organic solvents. Pioneering studies into solvent swelling were carried out by Stolow in the 1950s.^{53,93,224} An important objective of this research was the prediction of paint swelling from solvent properties.

It is surprising that the *solubility* model by Hansen^{231,232} and the simplified version by Teas²²⁹ were subsequently also used by the conservation community to predict *swelling*²³⁷ since these models were originally intended to describe dilute solutions of a polymer in a solvent. Solvent volume fractions during the swelling from dry polymer (no solvent) to equilibrium swollen polymer are much lower than in dilute solutions. Yet, describing swelling of oil paint using dilute solution theory has, despite the existence of theories specifically dedicated to polymer swelling such as Flory-Rehner, been a long tradition in

cleaning science.^{191,229,237,240} Consequently, it is not surprising that Zumbühl, having investigated 37 solvents and 75 solvent mixtures, came to the conclusion that no quantitative or qualitative prediction of solvent swelling was possible with the Teas chart.²⁴⁰ Stolow ranked the swelling capacity of solvents in oil paint and formulated a 'peak-swelling region' that was later plotted onto the Teas chart (see Figure 8.2).²³⁵ This approach was taken in order to minimise paint swelling and enable the conservator to choose solvent (mixtures) outside the peak-swelling region.²³⁵ However, the equilibrium swelling region for oil paint (grey area in Figure 8.2) as identified by Hedley²³⁵ using data from Stolow,⁹³ can shift depending of the paint type and age,¹⁷⁹ rendering the use of the Teas chart to predict swelling problematic. Figure 8.2 shows that the region for equilibrium swelling (also referred to as peak swelling or maximum swelling) can extend for different film types and by choosing a lower swelling capacity (light red area in Figure 8.2).²³⁷ Moreover, the region of equilibrium swelling (red region in Figure 8.2) was shown *not* to be located in a single zone as previously thought, but is composed instead of several sub-regions within that area, making it difficult to determine if a solvent will fall within the peak swelling region.²³⁷ It is remarkable that the Teas diagram was already heavily criticised more than three decades ago²³⁸ and is still shown today in recent publications.^{236,241,242} Recently, Zumbühl also reemphasised the limitations of the Teas chart.²⁴³

Several attempts have been made to classify the swelling capacity of paints in organic solvents into a practical model^{84,161,191,239,244,245} using more elaborate models than the Teas chart. However, these methods to predict paint swelling appear difficult to use, which may explain why the Teas diagram remains popular. Michalski¹⁶¹ presented a model that fits many solvents into a three dimensional 'egg-shaped' graph.¹⁶¹ However, some of the limitations of the Teas chart, such as the use of one parameter for both hydrogen donor and acceptor capacity are also inherent to Michalski's system²⁴⁰ and the models has not become widely used.

Zumbühl¹⁹¹ attempted to describe the equilibrium swelling capacity of 50 solvents on four types of artist paint using a combination of both δ_h and E_T^N with two solute-dependent factors used as 'fitting' parameters.¹⁹¹ Although his model is based on an adaptation of the Abraham model, which was shown to have good prediction power for dissolution,²²⁶ the results are not significantly better than the Teas chart at predicting the swelling power of solvents on oil paints. As shown in Figure 8.1a, swelling and leaching occur simultaneously and the dissolution of materials may influence the swelling capacity. Therefore, Zumbühl's study illustrates well that solubility *alone* does not capture the full complexity of the combined solvent action that occurs when oil paint is exposed to solvents.

Many researchers have attempted to correlate swelling to solvent properties since this would be convenient for practical cleaning purposes.⁹³ However, the prediction of swelling proved only successful in certain sub-classes of solvents, which is not surprising since all models described above have the fundamental shortcoming that they are solely

based on thermodynamics of solvent-solute interaction and do not account for polymer elasticity. A polymer swelling model accounting for polymer elasticity is the Flory-Rehner model, which is considered an accurate model to predict equilibrium swelling.^{246–248} This model is based on the force equilibrium between osmotic pressure due to swelling (entropy-driven) and the counter-acting elastic pressure. This model has never been applied to describe swelling in oil paint, but because it offers a straightforward manner to add the effect of polymer elasticity, describing swelling with Flory-Rehner theory is desirable.

Besides neglecting polymer elasticity in the description of swelling, oil paint cleaning literature does generally not distinguish between equilibrium swelling and swelling kinetics. As a result, solvent transport phenomena are not accounted for. Due to the limited contact times encountered in cleaning practice, equilibrium swelling is generally only reached in the upper-most layer of the paint. It is therefore necessary to investigate how the equilibrium swelling relates to factors such as the rate of solvent diffusion and leaching of soluble paint components. In general, models such as the Teas chart do not properly describe solvent action (Figure 8.1a) because they only consider thermodynamic (equilibrium) aspects of varnish solubility or equilibrium swelling of oil paint. They do not account for the *rates* of solvent swelling and desorption (due to evaporation and diffusion to the surface), and only poorly of solubility of internal paint components. Therefore, both thermodynamic aspects (such as solubility) and transport processes (such as solvent diffusion) should be modelled in order to get a complete theoretical description of solvent action. The feasibility of modelling these processes together is currently investigated by the authors.

Experimental swelling studies

The swelling of paint films in a range of solvents was studied by Browne^{82,249–257} in the 1950s, providing a useful classification of swelling power by type of solvent and pigment type. In a detailed study of swelling and leaching (see Section 8.6) Stolow found that the swelling curves obtained for films that had never been treated by solvents (referred to as 'virgin' films), differed from pre-leached films by the absence of a distinct equilibrium after about 10 min in the swelling curve (see Figure 8.3).⁹³ Virgin films showed a higher equilibrium swelling, reflecting the increased density of pre-leached samples, and turned out to be better reproducible.⁹³ These results indicate that swelling and leaching are strongly interconnected and that leaching may vary considerably, even between samples of the same composition.

Research has been carried out on the effects of solvent mixing on swelling behaviour. Mixtures are often used to decrease the 'rapid action' of some strong solvents, meaning solvents in which aged varnishes are highly soluble. Although the concentration of the high swelling solvent decreases when a solvent with lower swelling capacity is mixed

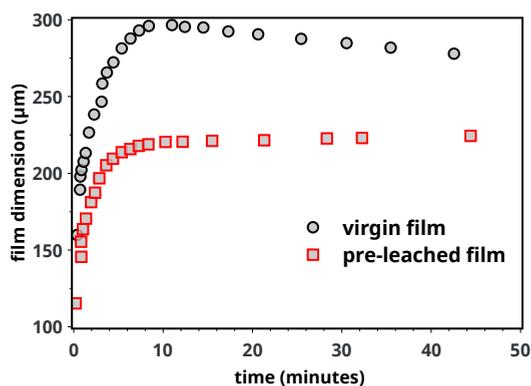


Figure 8.3 Swelling curve for virgin (unexposed) and pre-leached films, reproduced from Stolow.⁹³ The virgin films swells to a distinct equilibrium around 10 minutes and decreases in swelling at longer timescales due to leaching. The equilibrium swelling is higher in the virgin film indicating densification due to leaching in the pre-leached film.

in, mixtures of solvents may *increase* swelling capacity as compared to pure solvents. Figure 8.4 shows the swelling in binary solvent mixtures of benzene–n-hexane and acetone–isooctane. At the time, this phenomenon was rationalised in terms of a close match between the Hildebrand total solubility parameter²²⁸ of the mixture of solvents and the solubility parameter of the polymer (here considered as a solute).⁹³ However, Phenix¹⁷⁹ later argued that older paints chemically differ from the young paint used by Stolow, since the former contain higher concentrations of oxidised functional groups, which would lead to different polymer solubility parameters. We note that rationalisation of equilibrium swelling purely based on Hildebrand solubilities may indeed fail, as the underlying theory does not account for polymer properties, as done in Flory-Rehner theory.

More recently, Phenix systematically studied the swelling of unsupported paint films using a microscope.^{54,179} Special attention was given to the competing processes of swelling and leaching (see Section 8.6), which was found to be a major source of experimental errors. Phenix phrased this as follows: ‘The processes of swelling and leaching are, in some respects, in competition: an increase in the dimension of a paint sample due to solvent sorption may be more or less countered by the contraction associated with loss of binder matter.’⁵⁴ This is an important observation, because strongly leaching solvents may have a low(er) swelling power, which is often the case for highly polar solvents (except water). Large differences in degree of swelling between different paint films were also found: especially iron oxide earth pigments showed moderate to high swelling capacity. Exposure to light was found to result in a lower degree of equilibrium swelling and a slower rate of swelling compared to their unexposed counterparts, possibly due to increased cross-linking.⁵⁴ Another interpretation could be that light exposure results in more autoxidation of the oil and therefore more leaching and lower swelling.

We conclude that, although the exact reason for the differences in degree of swelling

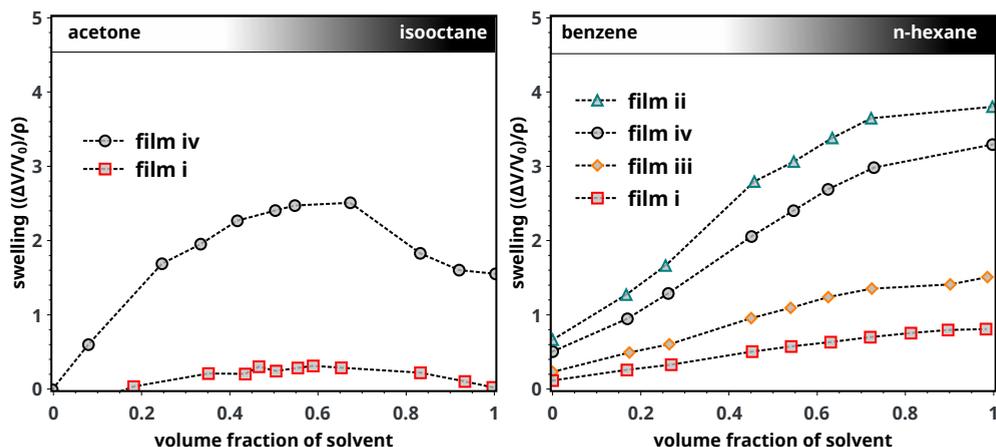


Figure 8.4 Mode of swelling in binary solvent mixtures of benzene–n-hexane and acetone–isooctane, reproduced from Stolor.⁹³ Film (i): vacuum stand oil and 0.5% lead naphthenate, 7 weeks at 32 °C; film (ii): vacuum stand oil and 0.5% lead naphthenate, 72 hours at 80 °C; film (iii): alkali refined linseed oil and 0.5% lead naphthenate, 72 hours at 80 °C; film (iv): open pot stand oil and white lead pigment, 18 weeks at 32 °C. All films were pre-leached in acetone (film i–iii) or methanol (film iv). Swelling capacity expressed as volume change ($\Delta V/V_0$) corrected for initial film density ρ (density before the experiment).

between different paint films was not always identified, it is again clear that the properties of the polymeric structure of the binding medium (Figure 8.1b,d,e) is a key factor that determines the swelling capacity of oil paints in organic solvents.

8.5.3 Solvent diffusion

The polymeric structure of the binding medium is again an important factor for solvent diffusion in paint. Diffusion is a form of solvent transport that occurs in the open space between crosslinked polymer chains, sometimes called the ‘inherent free volume of the polymer’.⁴⁴ According to Fick’s law, diffusion is described by a concentration gradient and a diffusion coefficient. When there is no significant interaction between the polymer and the solvent, the diffusion coefficient does not depend on concentration and one finds so called ideal Fickian diffusion. Whether deviations from ideal Fickian behaviour occur, depends on the rate of relaxation of polymer chains compared to that of diffusion. Such deviations are called non-Fickian diffusion, for which several theoretical descriptions are available.⁴⁴ In order to incorporate solvents, the polymer generally needs to swell to a certain extent, resulting in concentration dependency of the diffusion coefficient. The possibility for swelling will depend strongly on the concentration of crosslinks, which determines the elasticity of the polymer network. It should be noted that pure diffusive transport only occurs in intact polymer networks (Figure 8.1b,d,e). When cracks are present in the paint (Figure 8.1c), convective transport in cracks will also occur at rates

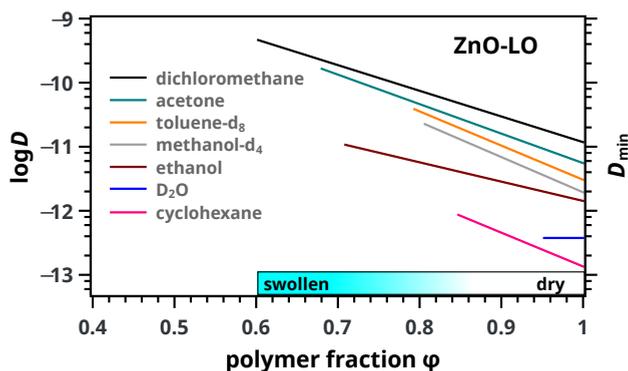


Figure 8.5 Diffusion coefficient in a pigmented ZnO and linseed oil based paint (ZnO-LO) versus polymer fraction Φ , calculated using the diffusion-swelling model. The diffusion coefficient increases during swelling (decreasing Φ).¹²²

orders of magnitude larger than purely diffusive transport.¹⁶¹

Recently, we used time-dependent ATR-FTIR spectroscopy to measure simultaneous solvent swelling and diffusion in model paint films.¹²² Such an IR spectroscopic approach, where solvent swelling and diffusion are measured at the same time, provides additional insights in how different processes during cleaning are interconnected (see Figure 8.1a). To quantify the spectroscopic data, a model was developed that describes the solvent diffusion process including significant film swelling and non-Fickian diffusion. This diffusion-swelling model describes the diffusion coefficient as an exponential function of the polymer volume fraction Φ , which is a measure of the swelling of the polymer. It was possible to estimate diffusion coefficients, which increased considerably during swelling (see Figure 8.5). One important finding was that strongly swelling solvents diffuse faster than weakly swelling solvents. The relation between diffusion coefficient (D_{eq}) and equilibrium swelling (f_{eq}) is displayed in Figure 8.6. The diffusion-swelling model also offers the possibility to predict the solvent penetration in paints exposed to typically short solvent treatments, as will be shown in forthcoming work. Equilibrium swelling could in principle be predicted using the Flory-Rehner equation if the Flory-Huggins interaction parameter (or Hildebrand solubility parameters) and the crosslink density of the network are known. Predictive models for the diffusion coefficient and its dependency on degree of swelling are virtually non-existent, underlining the practical relevance of accurately measuring these processes under controlled conditions.

The presence of pigments may influence solvent action. We studied the influence of ZnO pigmentation in the oil paint on swelling and diffusion and found no significant differences between pigmented and unpigmented films, likely due to relatively low PVC of $\approx 20\%$.¹²² Since the polymerised drying oil is the only component that swells, the diffusion coefficient of solvents and the degree of swelling is dependent on the amount of oil present in the paint.²¹⁵ Paints with a higher oil content (low PVC) will therefore show a higher

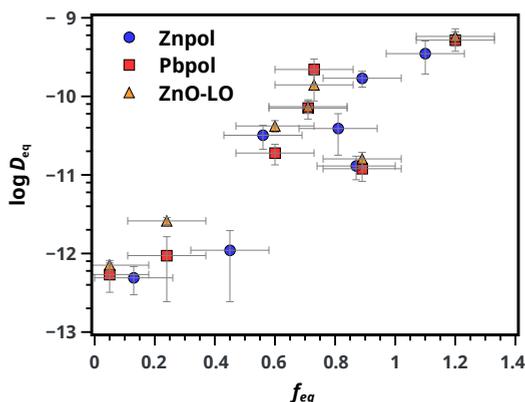


Figure 8.6 Correlation of equilibrium swelling factor, f_{eq} , with diffusion coefficient, D_{eq} for three types of linseed oil based model paints. Zn-pol: zinc ionomer, Pb-pol: lead ionomer and ZnO-LO: pigmented zinc white paint. Lower swelling generally shows slower diffusion.¹²²

degree of swelling given that they contain a similar network structure. Liu found that the diffusion coefficients of water diffusing through alkyd coatings initially decreased with increasing PVC, reaching a minimum value at 60%, and then increased with increasing PVC.⁵⁹ When the PVC was less than 60%, the barrier property of pigment was the main factor affecting the water diffusion behaviour. However, at PVC values greater than 60%, the formation of micro-voids around pigments allowed water to diffuse through these pores directly, leading to increasingly rapid diffusion.⁵⁹ Perera describes how PVC and water permeability depend on the presence of pigment-binder interactions. It was shown that a red lead (Pb_3O_4) alkyd paint became much less permeable to water with increasing PVC, which was attributed to the formation of lead soaps.²¹⁵ The permeability of a TiO_2 based alkyd paints was only weakly influenced by the PVC since TiO_2 hardly interacts with the binder.²¹⁵ These results illustrate how different polymer structures (Figure 8.1b–e) cause different diffusion behaviour, resulting in a different response to solvent-based cleaning.

8.6 Leaching

When solvents diffuse into a paint layer, leaching or extraction of soluble paint constituents will always occur to some extent but will mostly go unnoticed by a conservator during cleaning. Conservation scientists have studied leaching in considerable detail.^{83,112–114,171–173} Gas chromatography mass spectrometry (GC/MS) has often been used to determine the chemical composition of the leached materials.¹¹³ The primary concerns related to the leaching of oil paint are:

1. Embrittlement due to the extraction of low-molecular-weight (LMW) components,

which act as (secondary) plasticisers^{68,170,171,181,258–261}

2. Alteration of optical properties due to redistribution or removal of small molecules from the surface and formation of a surface haze^{198,262}
3. Disturbance of local chemical equilibrium which may lead to increased degradation reactions (see Section 8.8).¹⁴⁸

It is known that linseed oil-based paint films can significantly increase in density after exposure to organic solvents,⁹³ which has been attributed to the leaching of soluble components from the film. Depending on the age and type of film, up to 45 wt.% of the material could be leached by solvent immersion (see Figure 8.7).⁹³ Again, long leaching times of up to 120 hours make it difficult to assess the practical relevance of these particular results for cleaning. However, leaching also occurs with short exposure times. Realistic solvent exposure times were studied by Zumbühl, who investigated leaching in model paints using immersion times of 5, 10, 20 and 30 s.⁸³ It was concluded that with short interaction times, solvents with lower vapour pressure leached less material than solvents with a high vapour pressure.⁸³ The rationalisation given by Zumbühl using the vapour pressure on the leaching rate is problematic, as it confuses equilibrium thermodynamic effects with kinetic effects. Conducting experiments relating solvent vapour pressure to the rate of solvent diffusion, swelling, evaporation and dissolution are needed to investigate this effect.

The effects of leaching on the long-term physical stability of oil paint is not widely studied. However, short-term effects on the physical properties, such as paint stiffness, are more easily measured and more abundantly reported. The physical influence of solvent exposure on the viscoelastic properties of oil paint was investigated using dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC), which demonstrated that leaching results in embrittlement and densification of paint.^{31,68,219,259} It was found that polar solvents such as ethanol or acetone caused more embrittlement than apolar solvents such as cyclohexane with the same immersion time.^{68,259} Besides the differences in solubility of paint components in different solvents, this effect can be explained by the fact that ethanol or acetone are much faster diffusing solvents than cyclohexane,¹²² resulting in further solvent penetration and the extraction of larger amounts of plasticisers. An example of the embrittlement of paint due to solvent exposure is given in Figure 8.8, showing that 60 s immersion in acetone can induce a stronger increase in brittleness when compared to 126 days ageing at 50 °C.²⁶⁰ When a pre-leached paint was immersed in solvent after 25 years of natural ageing, renewed extraction of soluble components was observed.¹¹³ The continued leaching upon solvent exposure stresses the importance of considering oil paintings as metastable objects that continually undergo slow chemical alterations. Therefore, the disturbance of local chemical equilibrium by cleaning interventions may affect the rate of degradation processes and lead to unwanted chemical alterations on longer timescales. Such effects are discussed in Section 8.8.

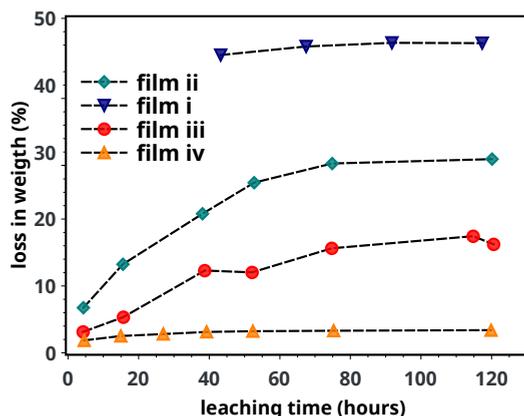


Figure 8.7 Leaching by weigh in different solvents, reproduced from Stolor.⁹³ Film (i): open pot stand oil, 30 weeks at 32 °C, methanol; film (ii): vacuum stand oil and 0.5% lead naphthenate, 30 weeks at 32 °C, methanol; film (iii): open pot stand oil, 17 hours at 80 °C, acetone; film (iv): open pot stand oil and white lead pigment (81 wt.%), 46 weeks at 32 °C, methanol.

The influence of leaching on the mechanical properties of oil paints have also been studied in real paintings. Using an NMR MOUSE¹⁸² (Mobile Universal Surface Explorer), Fife *et al.*¹⁷⁰ measured and compared the stiffness of two paintings from the same artist and time, one of which had never been cleaned and one that had been repeatedly exposed to organic solvents. The NMR MOUSE can be used for the non-destructive analysis of large objects and is used to measure the quantity of proton containing materials (amplitude, T_1) and the stiffness of the polymer network (rate of transverse relaxation time decay, T_2). In this study, it was shown that the painting that had undergone varnishing and numerous solvent-based varnish removals was significantly stiffer (larger T_2) throughout the depth of the painting.¹⁷⁰ This increased paint stiffness was attributed to the solvent-extraction of LMW components.¹⁷⁰ Since oil paint may also age differently in absence of varnish in the first place, it remains difficult to confirm to what extent the increased paint stiffness was indeed due to leaching. A major drawback of the NMR MOUSE as a tool in cleaning studies is the limited time- and depth resolution, which does not allow monitoring the uptake of rapidly diffusing solvents in thin paint layers. However, the magnitude of the transverse relaxation time before and after the cleaning procedure can be compared to reveal changes in brittleness.¹⁸¹ Prati *et al.* used this method to determine the influence of several green solvents (released by gels) on the stiffness of oil paints and found that γ -valerolactone and ethyl lactate can produce rapid and strong changes in the paint layer due to leaching.¹⁸¹ They also determined the retention of several solvents in paint, discussed in Section 8.7.

The chemical composition of the leached material (sometimes referred to as 'leachate') is generally used to evaluate the state of oil paint degradation. A large corpus of scientific literature is available on the composition of the leached materials.^{112,263–265} Due to the

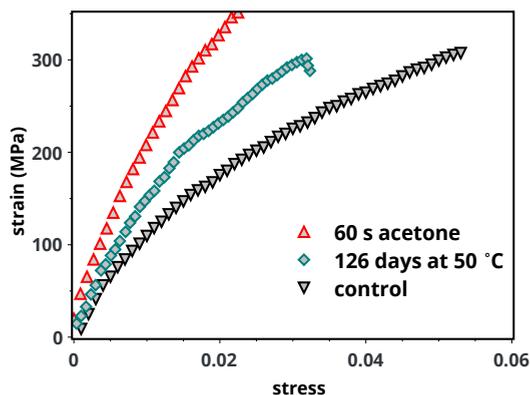


Figure 8.8 Stress versus strain plots of commercial titanium white paint made with alkali refined linseed oil, reproduced from Mecklenburg.²⁶⁰ The tests were conducted at 48% RH and 23 °C, after the paint had been exposed acetone for 60 s and allowed to dry.

complex autoxidation chemistry of unsaturated triglycerides, the composition of the leached material is complex and diverse. It is important to be aware of the assumptions most leaching studies make:

- characterising the extract (components *not* linked to the polymer network), provides accurate information on the autoxidation chemistry of the remaining polymer network
- more strongly degraded oil networks lead to more polar extractables.

Although these assumption have not been thoroughly investigated, recent studies suggest that there is indeed a correlation between degree of carboxylic acid formation⁸ within the network and an increased amount and polarity of extracted species.¹¹⁷ Nevertheless, it is important to realise that the information on the network structure from leaching experiments is obtained indirectly and may not reflect the combined influence of solvent action on the remaining polymerised oil network.

In most older leaching studies, pyrolysis gas chromatography mass spectrometry (Py-GC/MS) studies were carried out, which convert (derivatise) triacylglycerides (TAGs) into fatty acid methyl esters (FAMES). Derivatisation into FAMES is necessarily done in GC/MS experiments to detect the fragments. However, information on the size of the fragments is lost in the derivatisation: one does not observe intact TAGs or small polymeric fragments, only FAMES.^{120,264,265} The most abundant compounds found in extracts from oil paintings are carboxylic and dicarboxylic acids. In the autoxidation process of TAGs, cleavage of C16–C18 fragments leads to the formation of C8–C10 fragments. As a result, suberic (di-C8, octanedioic) acid, azelaic (di-C9, nonanedioic) acid, sebacic (di-C10, decanedioic) acid are often detected in addition to palmitic acid (C16:0) and stearic acid (C18:0).^{115,265} Due to the complexity of the leached materials, separation techniques such as liquid chromatography

(LC) are often used and combined with soft MS techniques such as electrospray ionization (ESI). Van Dam *et al.* used LC-ESI-MS to identify a great variety of oxidation compounds of TAGs.²⁶⁶ Modugno *et al.* used HPLC-ESI-MS to study the effects of relative humidity on the composition of extracts and found that ageing at high RH conditions resulted in increased extraction of dicarboxylic acids compared to ageing at low RH conditions.¹¹⁷ Following up on Van den Berg *et al.*,²⁶⁴ La Nasa *et al.* presented an analytical GC/MS method for the analysis of mixtures of free fatty acids and metal soaps in paint samples using selective silylating agents.¹¹⁶ This method can discriminate between regular free FAs and FAs derived from metal soaps using quantitative GC/MS analysis.¹¹⁶

It should be noted that the use of mass spectrometry to study paint extracts always leads to the detection of soluble paint components because mass spectrometry is incredibly sensitive. This sensitivity raises the important question when leaching becomes problematic, which is especially difficult to predict on longer timescales. In principle, it may be possible to extract non-crosslinked components from a paint without significantly altering the properties or physical stability of the polymer network. Therefore, leaching studies should ideally be combined with another measure of the effects of solvent action, such as chemical reactivity inside the remaining paint (see Section 8.8).

8.7 Solvent evaporation and retention

During solvent action, some solvent inevitably remains inside the paint layer for a certain period of time; this time is called retention time. The retention time of solvents is governed by the rate of solvent transport inside the paint and the rate of evaporation from the paint surface. Quantitative information on the retention time of common cleaning methods or solvents can contribute to better assess the risks associated with solvent cleaning.

Stolow showed that the rate of solvent sorption (k_S , uptake) is faster than desorption (k_D) and the two rates are related by $k_D/k_S \approx 0.65$ for all solvents except benzene.⁹³ This effect needs scientific attention. Nowadays, such effects can be predicted using theoretical modelling of solvent transport and evaporation in paint. Since the 1990s, work by Masschelein-Kleiner is frequently cited regarding solvent retention studies.¹⁸⁰ In this work, solvents were applied on mock-up paint samples and the retention time of a range of solvents was determined gravimetrically. Short retention times were found for the majority of saturated hydrocarbon solvents, as well as most halogenated solvents, benzene, toluene and ethyl- and isopropyl ethers.¹⁸⁰ More recently, solid phase microextraction (SPME) was used to determine the percentage of solvent retained in the paint after simulated cleaning treatments.¹⁹³ Combining SPME and NMR-MOUSE, Prati *et al.* showed the relation between paint softening and retention of solvent.¹⁸¹ Depending on the type of solvent, the presence of solvent could be detected with SPME for several hours up to several days, showing the long-lasting plasticising effect of highly retentive solvents such as benzyl alcohols. For some solvents, the stiffness of the paint after the solvent was fully

evaporated was shown to increase compared to the stiffness before solvent exposure, due to leaching.¹⁸¹

We recently used a newly developed portable Fourier transform laser speckle imaging (FT-LSI) setup to quantitatively study the dynamics of solvent penetration during cleaning at a high frame-rate.²⁶⁷ The FT-LSI setups allowed the study of solvent diffusion/evaporation rates and the total solvent retention time. In addition, qualitative spatial information on the spreading and homogeneity of the applied solvent was obtained. It was shown that LSI can detect the presence of ethanol in oil paint for more than 20 hours after saturation with solvent. In a series of measurements with increasing RH, a strong increase in dynamics at humidities above 40% was observed, underlining the great sensitivity of LSI for measuring solvent retention inside oil paints. A set of samples that was subjected to accelerated ageing at high RH were tested, as well as samples with different varnish thickness, different solvent application times, solvent application methods and a range of different solvents. It was found that solvents diffuse more in lateral direction and are retained in aged samples for a shorter period. Furthermore, it was found that varnishes temporarily hinder solvent diffusion into the paint. Different methods of solvent application showed different solvent retention and homogeneity after application.²⁶⁷

8.8 Solvent-mediated reactivity

The exposure of oil paint to solvents results in the penetration and retention of solvents inside the paint, which leads to paint swelling and the extraction of soluble paint components. Because solvents may be retained inside paint layers for prolonged periods of time, this raises the question what the influence of the presence of (small amounts of) solvents on chemical reactions inside the paint layer could be. This topic has been a central topic in our research group but received little attention by others. Apart from changes in physical properties of the paint bulk and optical properties at the surface, solvent action may result in the migration (redistribution) of soluble components between paint layers. The migration of soluble paint components can enhance the rate of degradation reactions inside oil paint when the paint is swollen with solvents. In order to understand the local chemical changes due to this migration process, it is important to understand the molecular mechanisms by which paintings degrade. The two most studied chemical processes in oil paint that could be affected by the use of solvents or water are: (1) hydrolysis of TAGs of the oil binder and (2) (crystalline) metal soap formation. Hydrolysis is an important pathway that leads to the release of high concentration of free SFAs in an oil paint. Alternatively, SFAs may be present as additives in modern oil paints or could have been added due to wax-resin lining with beeswax, which contains significant quantities of SFAs. If both high concentrations of free SFAs and metal ions are present, crystalline metal soaps are formed readily,²⁹ making hydrolysis and metal soap formation intimately related.

8.8.1 Fatty acid migration and metal soap formation

Crystalline metal soaps are a serious problem in oil paint conservation because they often lead to the formation of protrusions, crystalline material deposits on the surface and increased transparency of paint layers.³

To investigate if solvent-exposure can have an effect on slow chemical alterations in paint, we studied the effects of solvents on metal soap crystallisation in ion-containing linseed-oil based model systems.²⁹ These model systems mimic the situation where the common white pigments lead white ($2\text{PbCO}_3\text{Pb}(\text{OH})_2$) or zinc white (ZnO) have released lead or zinc ions into the binding medium and ionomeric metal carboxylates are formed.⁴³ These ionomeric metal carboxylates can exchange with SFAs to form crystalline metal soaps (complexes of metal ions and long chain saturated fatty acids). In our study, the reaction of ionomeric metal carboxylates with externally provided SFAs to form crystalline metal soaps was investigated in both pigmented and unpigmented (ionomer) model paints.²⁹ A custom-made reservoir containing SFAs dissolved in acetone was used to deliver the SFAs to the model paints. It was concluded that the exposure of ionomeric metal carboxylates to SFAs in solution is a sufficient condition for rapid metal soap formation. In addition, the transport rate of SFAs was found to be significantly enhanced by solvent-swelling and the presence of traces of water.²⁹ It was previously found that the rate of metal soap crystallisation decreases rapidly with the degree of linseed oil polymerisation, leading to amorphous metal soaps that are 'kinetically trapped in a semi-crystalline state'.⁷⁷ Even if no SFAs need to be displaced, it may therefore be possible that solvent swelling can also enhance the rate of metal soaps crystallisation by temporarily lowering the effective crosslink density due to swelling.

Knowing that solvent-swelling can lead to the migration and reaction of SFAs, we studied the extraction of a SFA marker (margaric acid, C17) and monitored the formation of zinc soaps as a measure of 'impact' of solvent cleaning.¹⁴⁸ Tailored bilayer model systems based on polymerised linseed oil, consisting of a C17 containing bottom-layer and a zinc ions containing top-layer, were used. Upon solvent exposure, the migration of C17 into the top-layer and subsequent metal soap formation could be tracked. Three methods of solvent application were compared: cotton swab, rigid gel and Evolon CR tissue (with different solvent loading).^{148,268} It was concluded that both swab cleaning and the application of Evolon CR tissue without controlled solvent loading, result in comparable SFA extraction. The rigid gel and Evolon CR with controlled solvent-loading limit the amount of SFA extraction.¹⁴⁸ Although redistribution of the C17 marker took place in all cases where solvent was applied, crystalline zinc soap formation was not observed after 5 min of ethanol exposure. In contrast, significant zinc soap formation was found after 30 min of ethanol exposure using Evolon CR tissue without controlled loading (see Figure 8.9).¹⁴⁸ These results show that the redistribution of SFAs between paint layers and their reaction with metal carboxylates to form crystalline metal soaps

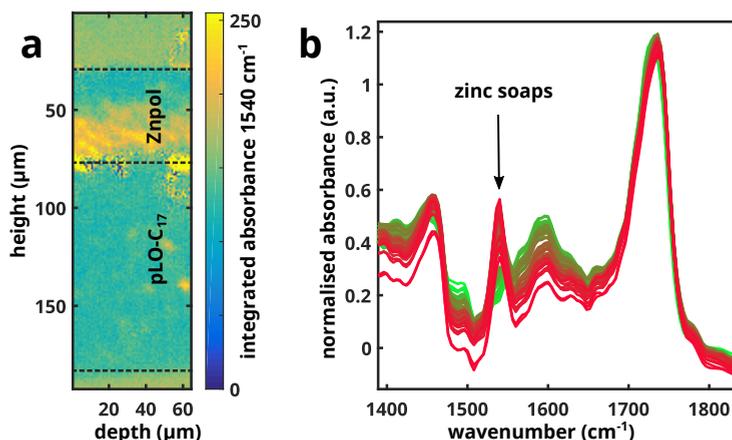


Figure 8.9 **a** Imaging ATR-FTIR map showing the distribution of crystalline zinc soaps (1540 cm^{-1}) in bilayer paint model after 30 min ethanol exposure using Evolon CR without controlled solvent loading. The zinc carboxylates containing top layers clearly showed the formation of zinc crystalline zinc soaps, which had been introduced by the SFA (C17) containing bottom layer due to ethanol exposure (direction of solvent flow indicated with arrow). **b** corresponding color-coded FTIR spectra: red is at the bottom of the zinc containing layer, green at the top. Image reproduced from.¹⁴⁸

can be enhanced by prolonged solvent exposure. However, it was also found that the differences observed after 5 min of solvent exposure using any of the studied methods did *not* lead to increased amounts of zinc soaps on longer timescales.¹⁴⁸ Compared to no solvent exposure in the blank, the differences in zinc soap formation were not significant 7 months after the experiments. These results show that the rate of SFA migration and zinc soap formation can be, even without solvent exposure, relatively fast if sufficient concentrations of free SFAs and zinc carboxylates are present. In that case, the influence of solvent exposure on zinc soap formation could not be detected.

8.8.2 Environmental humidity

Compared to the relatively stable environmental humidity conditions in museums,¹⁹⁰ the use of aqueous solutions for surface cleaning of paint results in high concentrations of water on relatively short timescales. It has thus far remained difficult to assess the risks involved with aqueous surface cleaning and how the risks of aqueous treatments compare to high RH conditions.

To investigate the effects of environmental conditions that likely promote ester hydrolysis in oil paint, the authors recently studied the effects of high RH on the autoxidation and ester hydrolysis in TAGs and the resulting formation of amorphous zinc carboxylates (COOZn).⁸ A strong increase in COOZn was observed at 77% RH compared to 12% RH due to an accelerating effect of water on autoxidation. No hydrolysis was observed under the conditions studied, suggesting that oil paints are, in the initial stage of curing, rather

resistant to hydrolysis. Considering the slow diffusion of pure water in oil paint²⁹ and comparably slow moisture diffusion alkyd paint,⁶¹ the moisture levels inside the paint layers at 77% RH for a week are likely more significant than the levels encountered during aqueous-based surface dirt removal. Therefore, the risks of enhancing the rate of hydrolysis of TAGs with the short exposure times typically used in aqueous cleaning methods, are likely to be limited. It should be noted that ester hydrolysis *alone* does not capture the full complexity of the risks involved with aqueous cleaning, which include possible pigment pickup and the solubility of organic dyes.

8.9 Modern materials for cleaning

Aiming for increasingly controlled application of solvents during cleaning, the focus of cleaning science has shifted from the measurement of swelling in the 1950s, towards the development and testing of solvents confined in emulsions and gels from the 1990s onwards.^{22,30,164,183,269–272} Thickened solvents and gelled systems aim to reduce the mechanical action necessary for surface cleaning and provide the conservator with 'superior kinetic control' of the cleaning process.^{273,274} In this context, gels are often called 'retentive', referring to the concept that they are supposed to retain the solvent more compared to a neat solution. The retention of the solvent inside paint is an entirely different phenomenon (Section 8.7). The confinement of solvents is thus proposed to reduce the rate of solvent diffusion into the paint, thereby limiting solvent action. With respect to the reduced solvent delivery rate by gels, it should be mentioned that one deals with two coupled solvent transport processes: one inside the gel, which determines the release rate of solvent by the gels, and one inside the paint. The relative rate of these two processes will determine if any 'superior kinetic control' compared to applying a pure solvent can be achieved with a gel.

Gels are commonly divided into two classes:

- Chemical gels, having covalent chemical bonds between monomers. These gels may come pre-made and only need soaking in the solvent of choice.
- Physical gels, having non-covalent interactions between monomers.^{164,275} These gels can either be mixed with solvent and spread on the surface directly, or come as powders that need to be mixed or heated to form the gel.

Physical gels are often called 'spreadable gel' or 'thickener' because they are applied by spreading them on the area to be cleaned. Examples of physical gels are Carbopol© (polyacrylic acid), Ethomeen© (coco amine ethoxylates), Pemulen© (copolymers of acrylic acid and alkyl acrylate crosslinked with allyl pentaerythritol) and polyvinyl-alcohol-Borax (often called moldable gels).^{22,31,95,276–278} These gels can be used with small amounts of water and the gel itself can have active cleaning properties. For example, the Pemulen© gels can

form oil-in-water (OiW) microemulsions with hydrocarbon solvents. The lipophilic part adsorbs at the oil-water interface and the hydrophilic part swells in the water forming a gel network. Although the phenomenon is not yet completely understood, the presence of both lipophilic and hydrophilic functional groups in one gel can enhance the cleaning properties compared to free solvents.

Polysaccharide-based gels belong to the oldest and most widely available gelling materials and are physical gels because they are held together by hydrogen bonds. Examples of polysaccharide-based gels are Gellan,²⁷⁹ agar,^{135,280} and Klucel® G, (hydroxypropyl cellulose). By increasing the concentration of agar in solution, the gel becomes more rigid and the pore size and rate of water diffusion decreases.²⁸¹ Because the diffusion of water is restricted²⁸¹ within the polymer network of these gelled systems, they can be used as slow releasing containers for the application of aqueous solutions. Although generally used with water, it is also possible to load polysaccharide gels with relatively polar solvents such as ethanol or acetone²⁸² or possibly with OiW microemulsions.²⁸³ Agar, and presumably other more rigid gels, can also be used graded by brushing small pieces of agar on an unvarnished paint surface.²⁸⁴

A disadvantage of physical gels is that they have to be cleared after application using free solvents and cotton swabs or sponges to avoid gel residues, thereby exposing the surface to additional solvent and mechanical action. Gel residues^{269,285} are hardly avoidable, especially for highly porous paints. Residue studies are an important part of cleaning studies dealing with the use of modern materials and it is generally assumed that residues should be avoided. However, the effects that residues may have on paint films in the future remain largely unknown, making this a particularly challenging topic in terms of risk assessment. Recently, an investigation of options for surface cleaning unvarnished water-sensitive oil paints was carried out, with particular attention to residues.¹¹ In one case, a correlation between traces of silicone emulsifiers and the formation of crystalline zinc soaps could be made based on ATR-FTIR analysis,¹¹ showing that silicone residues can increase the time that paints remains plasticised. It remains to be investigated if the prolonged plasticisation directly caused the increased formation of crystalline zinc soaps observed in the experiment. Strategies that aim to reduce gel residues by using polysaccharide gels loaded with cleaning solvent on an impregnation tissue and removing the gel with an absorbing tissue have been developed.¹⁹⁴ However, an additional clearance step is still required.

Chemical gels exhibit improved mechanical properties compared to physical gels; they can be shaped into a desired form and can swell in a liquid without gel solubilisation. Furthermore, the risk of having gel residues is reduced compared to physical gels due to the presence of covalent crosslinks.¹⁶⁴ Acrylamide-based chemical gels have been suggested as a residue-free alternative to the widely applied physical gel methodology.²⁸⁶ Semi-interpenetrating polyhydroxyethylmethacrylate (pHEMA) and polyvinylpyrrolidone (PVP) chemical gels (marketed as Nanorestore®) are polymer blends. Although

hydrogen bonds between the carbonyl group of PVP and the hydroxyl group of HEMA are present, the network consist of two types of linear polymers that are linked by covalent bonds.¹⁶⁴ Domingues *et al.* studied the water release of PVP/HEMA gels on paper by mass analysis and found that the water release of the newly developed rigid gels was significantly lower than that of the polyschararide gels agar and gellan (at 3 wt.%) or acrylamide based gels.²⁸⁷ It is important to note that although these gels were marketed for the use on painted surfaces, the water release was tested on a paper substrate, which will have a profound effect on the rate of solvent sorption by the surface. The higher 'retention' that was found may therefore be invalid for oil paint surfaces. One recent study used quasi-elastic neutron scattering (QENS) to study the polymer and water dynamics in pHEMA chemical and physical hydrogels at various water contents. It was found that, at a molecular level, physical gels show a slower water relaxation process compared to their chemical gel equivalents, likely as a result of side chains involvement in the formation of the three-dimensional network.²⁸⁸ It was not made explicit how this result translates to water release during practical gel application on painted surfaces. A comprehensive overview of novel materials and methods for cleaning is given in the in the Gels in the Conservation of Art conference proceedings book¹⁷⁶ and the book 'Nanotechnologies and Nanomaterials for Diagnostic, Conservation and Restoration of Cultural Heritage' by Baglioni *et al.*¹⁷⁵

The rate of water release by gels is not always lower compared to traditional methods of solvent application such as cotton swabs. NMR MOUSE experiments on acrylic emulsion paints showed that the amount of water delivered into the paint by agar gels was equal to swab cleaning. Other gels showed higher water release than swabs, which was often due to the need for a clearance step to avoid residues.¹⁸³ A similar conclusion was recently presented by Moretti *et al.*, concluding that NMR measurements collected before, during, and after wet-cleaning tests proved that the use of an aqueous Klucel© G gel did not significantly minimise the water penetration and swelling compared to swabs with free solvent.²⁸⁹ In contrast, combined mass analysis and NMR experiments on oil paint mock-ups demonstrated a decreased uptake of solvent by the paint when using gelled systems.¹⁷⁰ A decreased release of solvent to the paint surface compared to swabbing was also found using ethyl lactate confined in a polyhydroxybutyrate gel.¹⁸¹ It thus seems that there are considerable differences in the rate of solvent uptake in paint when using gels, which is likely explained by the variation in solvent transport rates expected in different polymerised oil networks (Figure 8.1b–d) encountered in paintings.

In this context, the authors used time-dependent ATR-FTIR to study the kinetics of solvent delivery of three cleaning gels on model systems for intact oil pant binding media.³² These model systems were polymers based on a polymerised linseed oil matrix with Zn^{2+} and Pb^{2+} ions included as an integral part of the network; similar to aged oil binding medium in paintings without cracks (for example Figure 8.1b).^{42,43} The diffusion of organic solvents and water into linseed oil based ionomers was found to be of similar

magnitude for both free solvents and solvents released by gels, indicating that the solvent uptake by non-porous linseed oil based ionomers is relatively slow compared to the rate of solvent release by the gels.³² This result demonstrates that the advantages of gel cleaning in terms of reduced solvent uptake by the paint are strongly dependent on the surface that is cleaned and the application time. When only judging solvent delivery rate inside the paint, the largest benefit of the use of gels is likely when cleaning porous substrates with a short application time. However, the advantages of reduced mechanical action of gels compared to swab cleaning remain relevant on any substrate.

8.10 Conclusions and outlook

The use of organic solvents on oil paint surfaces causes simultaneous solvent swelling, –diffusion, –evaporation, –leaching and solvent-induced chemical reactions, altogether defined as solvent action. Solvent action on oil paint includes both temporary chemical and physical changes, such as swelling and an increase in the rate of FA migration and metal soap formation, as well as permanent changes, such as the leaching of LMW components, or an increase in the brittleness of the paint. Using the words of Gilson, both *cleaning* and *not cleaning* are ways to ‘let a painting perish’. Therefore, the only way to resolve this dilemma is to work towards a reliable assessment of the risks involved in cleaning by creating a thorough understanding of the physicochemical process involved in solvent action.

We discussed the processes that play a role in solvent action and presented the current status in the theoretical description of these processes. It was explained that cleaning often involves a complex mix of these processes, which nevertheless deserve separate theoretical descriptions. Although literature from polymer chemistry can be of great relevance for studying solvent action, not all areas in cleaning science have absorbed proper knowledge from the scientific community outside art conservation. Solubility theory is well accounted for and is adequately applied to dilute solutions. However, we conclude that the important phenomenon of paint swelling, which requires accounting for polymer properties, is not yet addressed using state-of-the-art theory and recommend the Flory-Rehner model to describe equilibrium swelling. Moreover, equilibrium swelling and swelling kinetics are often not distinguished. Swelling kinetics demands simultaneous treatment of swelling and diffusion. We recently developed a swelling-diffusion model that can provide the theoretical basis to additionally simulate leaching, evaporation and solvent retention based on the knowledge of swelling and diffusion in paint films. To start describing solvent action in the future, the swelling-diffusion model should be combined with models for mass transport across the paint surface using thermodynamic models describing the vapour- and liquid-liquid equilibrium at the surface.

Although solvent action is very complex, the processes involved in solvent action are directly linked to the properties of the polymeric oil binding medium. The chemical

and physical properties of this polymer depend on the material composition and the environmental conditions during the drying and ageing of the paint. In cleaning science, polymer properties of the binding medium are often discussed in terms of solvents sensitivity. However, solvents sensitivity is merely a manifestation of influence of (in)organic pigments on the autoxidation chemistry of the oil, resulting in various types of polymeric binding media. These types of polymeric binding media determine to what extent solvent action can occur during cleaning treatments. Cleaning research could therefore focus on techniques that can relate polymer properties of the binding medium to solvent transport processes. Both theoretical and experimental work is needed to further develop the relation between polymeric structure and solvent action and estimate when solvent exposure may lead to unacceptable risks.

To advance our understanding of solvent action on the molecular level, analytical methods that can monitor the possible changes in chemical composition of an oil paint upon solvent exposure are required. Ideally, one would combine quantitative and spatially-resolved information on solvent transport with chemical information on reactivity. Such an experiment may be possible with time-dependent FTIR imaging in transmission mode, where both solvents and potential degradation products are measured quantitatively and spatially-resolved. In order to integrate forthcoming cleaning research more closely into conservation practice, the focus should be on developing methods to monitor cleaning action in *real time*. To enable a comparison of cleaning methods or solvents on real paintings, these methods should be quantitative, portable and able to deal with heterogeneous paint surfaces. In addition, the instrumentation should feature an intuitive interface and should be easy to operate for conservators. Lastly but very importantly, data processing and interpretation should be fast (preferably on-the-fly) and should not require a software programming background. As an example, FT-LSI was presented as a powerful, quantitative and portable imaging technique for the study of solvent retention during oil paint cleaning and showed its potential for future use in the conservation studio.

The large number of publications focusing on novel materials for solvent application have provided important insights that can result in a reduction of the amount of solvent that is needed for cleaning. These materials can be used to their full advantage when the solvent diffusion rate out of the gel is the rate limiting factor. This is the case for porous and cracked paint surfaces where solvent transport inside the paint will be fast compared to solvent release by the gel. The potential of gelled systems to reduce mechanical action can provide an added benefit on any paint surface. In the development of novel materials for cleaning, gelled systems that allow precise tuning of solvent polarity are greatly desirable. To that end, gels with increased capacity for apolar solvents or microemulsions containing largely apolar solvents could be further developed or adopted from other fields such as cosmetics or coatings industries.

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