

Review

The Usefulness of Infrared Spectroscopy for Elucidating the Degradation Mechanism of Metal Industrial Heritage Coatings

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Abstract: As society moves away from heavy industry, large metallic structures will be abandoned. As an alternative to dismantling, these structures could be repurposed. Beyond being a practical solution, the conservation of these structures would serve as an ode to the role of these industries in shaping modern society. Conservation, however, requires suitable coatings that hinder corrosion long-term while not significantly altering the outward appearance. Traditionally, the stability of coatings has been tested by comparing fresh samples to those aged naturally or in a UV chamber. This method of testing provides no temporal information. Additionally, measuring many different conditions, e.g., UV, humidity, temperature, and pollutants, is tedious. In this review, we highlight how by implementing infrared spectroscopy in different configurations, temporally resolved information about the coating chemistry, the metal–coating interface chemistry, and gas emissions could be gained during degradation. These insights would be essential to enable the intentional design of coatings while simultaneously revealing their environmental impact.

Keywords: organic coatings; infrared spectroscopy; photodegradation



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1. Introduction

Metallic corrosion poses a significant economic burden, with annual costs in the United States alone estimated at USD 276 billion [1]. This burden will be further exacerbated with the transition from certain heavy industries. In the future, large, abandoned steel structures and empty facilities will be left behind. Ensuing issues are exemplified by coal coking plants, which were once essential for turning coal into metallurgical coke needed for steel manufacturing. Due to environmental concerns, alternatives to coke are being pursued. Most coking plants in the USA and Europe are now over a century old, and even the few plants still in operation have begun to decay structurally. The Bluestone Coke Plant in North Birmingham, Alabama, is a particularly critical example. In 2020, the metal doors fronting the 1800 °C ovens in which coal was distilled to coke had heavily corroded. As a result, the previously contained toxic chemicals leaked out at an accelerated rate into nearby neighborhoods. The plant has since closed but continues to garner criticism for the uncontrolled release of contaminants into the environment [2]. Clearly, simply ignoring corrosion can have devastating results.

As of today, most plants have or are slated to close. One alternative would be to systematically dismantle them. The 2018 planned implosion of smokestacks at the Shenango Coke Works on Neville Island in Michigan is a poignant example of the challenges of dismantling. The demolition was only possible after eliminating environmentally hazardous materials and with proper precautions to limit dust formation [3]. Due to the challenges and dangers of demolition, finding ways to prevent the decay of these large facilities and enable their repurposing would be highly beneficial.

Beyond the practical advantages of conservation, these heavy industries left an indelible imprint on modern society. Coal mining, for example, often strongly influenced the

culture of the surrounding regions. As a result, some structures clearly have significant historical value [4]. Prominent examples have already received protected status. The Zeche Zollverein Coking Plant in Bochum, Germany, shown in Figure 1a, was declared a UNESCO World Heritage Site. Also, in the United States, industrial buildings have been successfully repurposed, examples being the National Museum of Industrial History, which is housed in former buildings of the Bethlehem Steel Mill in Pennsylvania, and the National Historic Landmark Sloss Furnaces in Birmingham, Alabama, depicted in Figure 1b.



Figure 1. (a) Aerial image of the Zeche Zollverein in Bochum, Germany. (b) Sloss Furnaces in Birmingham, Alabama, USA.

To preserve these industrial monuments for future generations and to enable their repurposing, anticorrosion coatings are needed. Generally, coatings act as barriers that hinder the reaction between agents of corrosion such as moisture, oxygen, and pollutants, with the underlying metals. Suitability for industrial heritage conservation requires that the coatings are visually non-intrusive, have low toxicity, are easily applied, and are stable in outdoor environments [5]. Many seemingly suitable clear coatings undergo undesired photocatalyzed changes over time, e.g., become opaque and/or lose their anti-corrosion functionality. There will also not likely be a single ideal coating for all monuments, as the degradation is highly dependent on the initial state of the structure. As a result, corrosion products or remnants of prior coatings on the surface will likely influence the effectiveness of the new coating. Furthermore, due to the vast area of these monuments, for example, the Zeche Zollverein encompasses 100 hectares, the long-term environmental impact must be considered. This requires caution during manufacturing, but also a thorough understanding of any emissions that occur during the service time of the coating.

Over the last decade, increased stability and lowered toxicity have driven coating research. Many variables must be considered when testing coating stability, i.e., the nature of the metal, changes in humidity, pollutants, and ultraviolet (UV) exposure. Generally, the stability of coatings is tested ex-situ by comparing fresh samples to those either aged naturally or in large UV chambers. The major limitations of ex-situ studies are the lack of time-resolved information and the limited flexibility, as all samples are aged in the same atmosphere. As a result, the large-scale testing of many samples under different conditions is time and labor-intensive. Most studies only consider a limited number of samples or conditions, which has resulted in an incomplete understanding of the degradation mechanism [6]. More systematic studies that explore a full matrix of variables are needed. Ideally, methods are needed that allow samples to be studied continuously during degradation. In this review, we focus on the versatility of infrared (IR) spectroscopy for studying the chemistry of coating degradation. We conclude that if applied in different configurations, in-situ IR measurements could provide the necessary temporal evolution of coating degradation chemistry. With a better understanding of the degradation mechanism, it will become possible to intentionally design more suitable coatings and to better predict their long-term environmental impacts.

2. Coating Studies

In general, the coating lifecycle can be divided into three major stages, the materials manufacturing stage, the in-service period, and the disposal, as depicted in Figure 2 [7]. Different aging conditions are known to influence degradation and thus must be considered, specifically moisture, air pollution, and UV radiation. To be suitable for use in metal industrial heritage, coatings must show sufficient stability in the expected conditions. This is especially challenging for industrial heritage conservation as the coatings should not be visually intrusive to maintain historical integrity. As a result, UV adsorbing pigments cannot be added and photodegradation presents a significant challenge. Coating degradation depends on the coating type, surface (smooth or rough), exposure conditions, coating application, and number of layers [8]. These dependencies further complicate the selection of heritage coatings, as different structures will have been exposed to different environments during use and as a result, will have highly variable starting conditions. Information about the interface between the coating and the artifact would be needed.

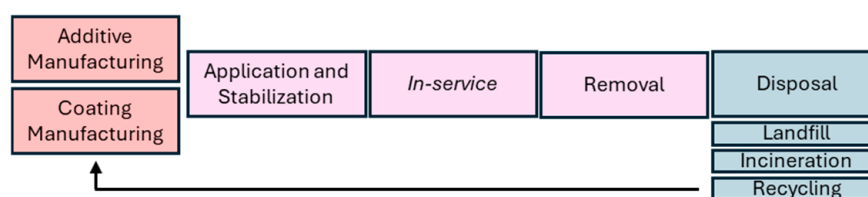


Figure 2. Schematic showing the stages in the lifecycle of a coating. This is a graphical summary of the stages described by OECD in their report [7].

In addition to being key for preventing further corrosion of the artifact, stability must be ensured to hinder significant environmental effects. Pollutants from the coatings can end up in the air, water, and soil [7]. For most coatings, negative environmental impacts are largely considered to occur during the manufacturing process [7]. Nonetheless, recent studies have reported problematic emissions from plastic articles when they are exposed to ordinary levels of sunlight, heat, and moisture [9,10]. In order to fully elucidate the environmental effects, emissions during all stages of the life cycle should be considered. Here we highlight how IR spectroscopy can be used to better understand the degradation mechanisms of coatings and to model in-service gaseous emissions.

2.1. Sample Preparation

Overall, the application of coatings on heritage metals is poorly standardized, which makes comparison between studies difficult. In the following section, we explain the procedure suggested by Molina et al. as a new standard [11]. To prepare the surface, metal coupons should be cut and sanded with grit emery paper followed by ethanol cleaning. The coatings can be applied using different methods ranging from brushing, spraying, dipping, etc., as long as the method and the parameters are clearly defined. As the coating application is typically applied by hand, reproducibility must be verified. The samples should, therefore, be prepared in triplicates. In the case of multilayers, each layer should be allowed to dry for 48 h before additional layers are applied. Even with this standardization, differences between samples can exist. It was found that not only can the number of applied layers influence the film thickness and protective strength, but the total drying time must also be considered [11].

This standardization was created for the testing of coatings on metal coupons. Clearly, when applying the protective layer to real historical objects, the sample preparation process is dependent on the condition and stability of the artifact [12].

2.2. Ageing

The best practices for studying stability have been laid out by the American Coatings Association. To establish the stability of coatings, reliable accelerated testing must have (1) a controlled amount of UV and visible radiation at the specimen surface, (2) controlled

temperature, (3) and humidity [13]. Artificial aging lasts for weeks or months, while natural aging can last from months to years [14]. This aging technique can be accelerated by using amplified adverse conditions (sun, heat, cold, salts, vibrations) in combination with environmental factors such as UV exposure, temperature, relative humidity, and pollutants ozone, NO_x , etc. [15]. After sample preparation, coated metals are subjected to artificial aging tests in UV chambers that mimic outdoor atmospheric conditions. Different conditions encompassing condensation, temperature, and UV light at varying residence times must be studied as aging mechanisms can behave synergistically.

Although existing standards such as ISO or ASTM have not usually been adapted to heritage studies, they should be used to guide tailored and more standardized tests [11]. Molina et al. carried out their tests at alternating cycles with 340 nm UV-A light and condensation at 50 °C according to ISO 4892:3 [11]. ASTM D5894, also known as Cyclic Salt Fog/UV Exposure of Painted Metal Test provides a standard for aging. ASTM G155 also outlines accelerated aging on a wide range of products and industries, including products for the automotive industry, surface coatings, rubber, adhesives, and textiles [15].

Aging processes increase as a function of ambient temperature. As a simplification, the Arrhenius law is often considered to govern the acceleration process. For example, the generation rate of CO_2 during the photooxidation of the polymer polypropylene was monitored using gaseous transmission IR spectroscopy. It was found that in the measured application, the relevant temperature region (30–80 °C) and the CO_2 generation rate followed the Arrhenius law [14]. The value of the attained activation energy within this region led the authors to conclude that polymer decomposition is dominated by a single chemical process [14]. As a rule of thumb for most chemical reactions, the reaction rate doubles when the temperature increases by 10 °C [15]. If the degradation process were diffusion-limited, a shallower slope would be expected in the Arrhenius plot. Furthermore, if a too-high testing temperature is selected, chemical reactions with higher activation energy could begin to occur that are not significant during the natural aging of the coatings. Even to simulate longer periods of time in extremely adverse conditions, excessive temperature is therefore not recommended [15].

2.3. Standard Analysis

Coatings are often evaluated by electrochemical impedance spectroscopy (EIS) and a novel electrochemical cell has been developed for in-service measurements [16]. Most other studies are conducted ex-situ, i.e., the coating is studied before and after aging. The homogeneity and appearance of the coatings are usually studied with visual inspection or with optical microscopy [11]. More detailed morphological information is gained using scanning electron microscopy [17]. Changes in the glossiness of the coatings have also been analyzed as an indication of coating stability [18]. Hydrophobicity variation is probed using contact angle measurements [19]. Corrosion products are identified with Raman spectroscopy [11]. To gain information about chemical changes in the coatings, both X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR) are used [20]. The samples are studied under vacuum, XPS, however, is ill-suited for in-situ studies. IR spectroscopy has no such requirement. By using IR in different configurations, complementary information about emission products, surface chemistry, and insights into changes at the metal–coating interface could be gained. In the following section, we will provide more information about IR spectroscopy in general and how it could best be applied to study coating degradation.

3. Infrared Spectroscopy

The functional properties and durability of coating polymers largely depend on their chemical structure, which can be probed using IR spectroscopy [21]. In IR spectroscopy, the sample is typically irradiated with light within a wavelength range of between 2.5 mm and 15 mm (wavenumber 4000 cm^{-1} and 666 cm^{-1}). At specific frequencies, bonds within the coating are excited and begin to vibrate. If the molecular dipole moment changes during the vibration, then it is IR-active. The characteristic frequency of a bond is related to the

chemical structure, relative atomic weights, spatial position of atoms in a molecule, and intra- and intermolecular interaction forces [22]. Some of the most common vibrational movements include asymmetrical/symmetrical stretching, scissoring, twisting, rocking, and wagging [22].

IR spectroscopy can be applied in different configurations. As a result, in addition to understanding the chemistry of the coating during degradation, it would also be possible to gain information about gaseous emissions during aging or to detect changes in the metal–coating interface. In the following section, we will describe different configurations in more detail. We will describe how IR can be applied to study coating degradation. As these terms are used differently across fields, we will define what is meant here by ex-situ, in-situ, and in-service. For clarification, ex-situ refers to studies in which representative samples are studied in non-application-relevant conditions. Examples of ex-situ measurements would be transmission IR conducted on coating samples before and after aging that have been diluted in KBr. In-situ is used to describe work conducted on coatings applied to a representative metal layer that are studied while under conditions mimicking those expected in the heritage conservation application. This could be coatings applied to a metal coupon or coating on thin-film metal layers, which are studied while being aged in atmospheric control chambers with UV light. Finally, in-service measurements are conducted directly on layers applied to monuments or monument components and are non-destructive. This could include measurements directly on monuments or measurements conducted in the lab on artifacts that can be returned to the heritage site. We make this differentiation to indicate measurements that could be conducted repeatedly on real artifacts.

3.1. Transmission

Transmission is the most widely used configuration and provides information about the overall chemistry of the sample. In this configuration, first introduced in 1952, the IR light passes through a sample [23]. As a result, the solid samples must be sufficiently transparent to allow for detection. The typically strongly absorbing polymer coatings must therefore be diluted using IR transparent materials such as KBr or NaCl (Figure 3a). Alternatively, extremely thin layers (~5–10 µm) have been successfully used (Figure 3b) [24]. In both cases, the transmission IR spectra of the coating before and after degradation are compared.

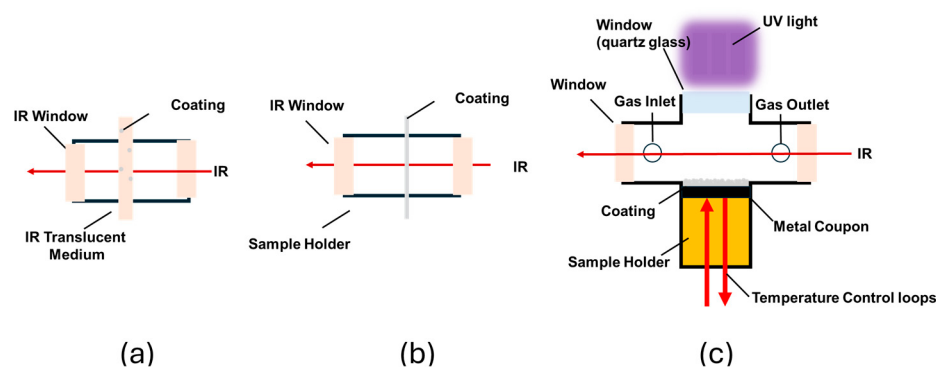


Figure 3. Set-up of IR translucent chambers used in transmission mode for (a) diluted coatings pressed in pellets of translucent material, (b) thin coatings, and (c) testing gas emissions from coatings during photodegradation.

The transmission configuration can also be used to detect the generation of volatiles and gaseous products produced during aging. A sealable aging cell that allows for heating and UV irradiation of a sample under a controlled environment during the simultaneous detection of any atmospheric changes using transmission IR is shown schematically in Figure 3c. In this in-situ cell, a Xenon arc lamp is used for irradiation. Using such a setup, the emission of CO₂ was successfully monitored in-situ during the photo-oxidation of polypropylene (PP) polymers [14]. During the degradation of nitrile rubbers, the emission

of volatile species was identified by increased absorption at wavenumbers characteristic of C-H, C-N, and -N=C=S- bonds [25]. Overall, it was found that the weathering results attained in the in-situ chamber have good correlation with natural weathering [14].

3.2. Attenuated Total Reflection (ATR)

The technique of internal reflection spectroscopy, also called attenuated total reflection (ATR), was introduced in the early 1960s [26]. It is popular as almost any material—solid, powder, or liquid—can be easily and nondestructively analyzed. ATR relies on complete reflection during the transition from an optically denser medium or crystal to a thinner medium. The sample is placed in direct contact with an ATR crystal, typically made of diamond, germanium, silicon, or ZnSe. The crystal wall directs the radiation beam to the interface with the sample at an angle, which results in complete reflection at the internal crystal side. In the simplest case, the reflected beam then comes out through the second crystal wall and the beam intensity is recorded. The total internal reflection results in an evanescent wave whose perpendicular components interact with the optically thinner medium. See the schematic in Figure 4 [22].

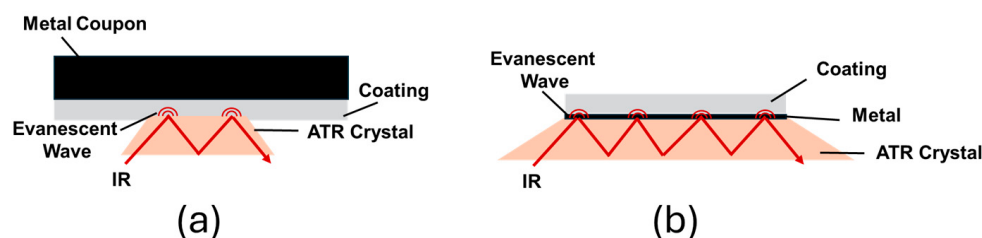


Figure 4. Schematics depicting the ATR configuration using (a) a crystal that is contacted to the coating surface compared to (b) the Kretschmann configuration in which the interface between the coating and the metal is probed.

For ex-situ studies, an ATR crystal is brought into contact with the coating surface before and after aging in a UV chamber. The IR evanescent wave penetrates the sample surface layer (~0.5–5 μm) (see schematic in Figure 4a) [22]. Many modern IR microscopes have an ATR crystal add-on, making this kind of ex-situ measurement of the coating surface readily available. ATR measurements conducted directly on the metal artifact surface allow corrosion products to be non-destructively detected [27]. Additionally, ATR could be used to identify the chemical composition of coating remnants found on the metal surface. The ATR-IR spectral databank of many heritage artifacts, including coatings and paints of Vahur et al., could be useful for identifying what the remnant coating is [28]. This information would be useful for better understanding the interface that forms between the monument surface and the newly applied coating.

In the Kretschmann configuration, ATR can be used to study changes in-situ on model systems at the metal–polymer interface (Figure 4b) [29]. Despite the absorbing character of metals, an electric field can pass through a thin metal film. If the thin metal film deposited (~tens of nm) on an ATR crystal is coated with a polymer film, the evanescent wave can probe the metal–polymer interfacial region [30]. In this way, ATR has been successfully combined with impedance spectroscopy to study water uptake and diffusion in polymer films [29]. This configuration could be used to gain information about the interaction between different metals and coatings.

3.3. Photoacoustics

In photoacoustic IR, the absorbance of the impinging light beam alters the thermal state of the sample (Figure 5). By modulating the light periodically, the absorbing sample warms and cools cyclically. The solid sample is usually contained in a gas-tight cell that is filled with helium, and the thermal expansion results in acoustic pressure oscillations. As the frequency of modulation of the source corresponds to the audio region, sound waves are generated. The sound wave can be detected by sensitive microphones, piezoelectric

devices, or optically. Depending on the frequency, different depths (0.1–100 μm) of optically transparent samples can be studied [31]. Simplistically, the slower the modulation the further the heat can move through the sample [32].

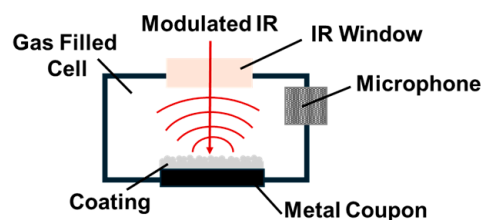


Figure 5. Schematic of a cell used to study the degradation of coatings via photoacoustic IR.

Although less common than the other configurations, there are several studies in which photoacoustic IR was used to study the degradation of paints and organic coatings [26,33]. The advantages of photoacoustic IR are that sample preparation is not necessary, it is possible to study different surface depths, and the method is non-destructive [34]. The main disadvantage is that it cannot be readily used to study the coating chemistry in-situ, as variations in the gaseous environment strongly influence the measurement [33].

3.4. Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

DRIFT spectroscopy offers a direct and non-destructive method for the identification of coating materials and binders [35]. In DRIFT spectroscopy, light is reflected at numerous angles that are not equal to the incident angle on a porous surface. See Figure 6 [26]. The measurement utilizes optics that are designed to reject specularly reflected radiation while collecting as much of the diffusely reflected light as possible. It is suitable for recording opaque and scattering samples with or without sample preparation [21]. DRIFT spectroscopy is known to be much more surface-specific than other IR configurations [36].

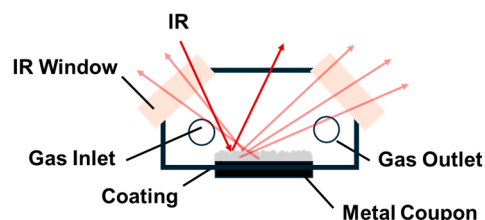


Figure 6. Schematic of a DRIFT spectroscopy cell used to study coatings in controlled atmospheres.

Pandey and Kumar used DRIFT spectroscopy to differentiate between coatings on aluminum [21]. There are several studies in which the aging of wood under UV over time was conducted using DRIFT spectroscopy [37]. As the coating chemistry can be probed and the method can be used to detect changes as a result of UV degradation, it is likely that by adjusting the window configuration of the atmospheric transmission cell (Figure 3c), useful insights could be gained from in-situ DRIFT measurements.

4. Industrial Heritage Coatings

No single coating is suitable for all metal surfaces and all heritage environments [6]. The largest hurdle for industrial heritage conservation is the degradation of the initially clear coatings due to photo-oxidation. Photo-oxidation is influenced by physical and chemical weathering during irradiation in the presence of oxygen, water, and temperature variation. This degradation is especially challenging for heritage conservation, as it is typically suppressed by adding an adsorbing pigment, which is not possible when a clear coating is desired. Degradation can cause the once-clear coating to become cloudy or discolored, thereby changing the appearance of the artifact. Furthermore, due to the large nature of industrial heritage conservation structures, it must be proactively ensured that coating degradation does not result in environmental hazards.

Different coatings have different chemistries, which dictate their stability. Over the course of decades, increased stability requirements and environmental concerns have driven coating research [1,6]. In the section below, we will discuss coatings that have been historically used, as well as novel coating chemistries. We give examples of how IR spectroscopy has been successfully applied to study the interaction between the coating and the metal surface and has helped unravel photodegradation.

4.1. Waxes

Metal coatings were already developed in the seventeenth century. They were made of turpentine solvent and linseed oil binder in addition to white lead pigments and additives. Others included coal tar and bitumen [6]. These coatings were mostly applied on functional structures, e.g., bridges. Oils and waxes were also historically used on ironworks [8]. Wax's protective function has been attributed to its ability to exclude moisture and oxygen from the metal surface [38]. Generally, waxes are made up of esters of a long-chain alcohol and a long-chain fatty acid [39]. The IR bands associated with waxes are between $3000\text{--}2800\text{ cm}^{-1}$ for the C-H stretch, $1480\text{--}1350\text{ cm}^{-1}$ for the C-H bend, $1790\text{--}1600\text{ cm}^{-1}$ for the C=O stretch, and $1300\text{--}1100\text{ cm}^{-1}$ for the C-O-C. See Figure 7 [40].

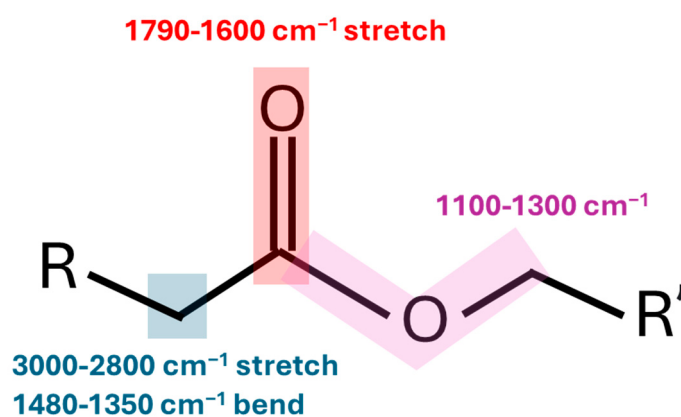


Figure 7. Schematic of the general chemical formula for waxes. The expected IR band regions are based on the work of Swartz et al. [40].

4.1.1. Degradation and Challenges

The use of waxes continued, and in the 1970s, polyethylene waxes were widely used in mixtures with microcrystalline waxes by the US National Park Service for outdoor monument conservation [41]. In the subsequent decades, however, it was found that waxes showed low weathering resistance and needed to be renewed frequently. In some cases, it was even found that due to their porosity, wax coatings accelerated corrosion by retaining contact between the metal surface and a corrosive solution [42]. When exposed to sunlight, especially the UV component, waxes have been found to undergo oxidative degradation, resulting in hydroxyl group formation associated with a higher n-alcohol content [40]. This degradation mechanism is most pronounced at the surface of the wax. In ex-situ ATR measurements of artificially aged wax samples, it was found that the bands associated with fatty acid esters, 1736 cm^{-1} and 1171 cm^{-1} , decreased, while there was an increase at 1720 cm^{-1} , which was attributed to free fatty acid formation [43]. This chemical change alters the material properties, e.g., brittleness, hardening, and color changes. Over the lifetime of the coating, grainy crystals form [44]. In addition to temperature variations, it has been proposed that a driving force for changed film crystallinity is the exclusion of branches from the majority of linear alkanes' crystalline phases [40]. Periodically, an aesthetically unpleasing white crystalline efflorescence, commonly called "wax bloom", appears on the surface of wax coatings [45]. Although efflorescence has been widely reported, its origin is poorly understood [46]. Wax coatings are typically assumed to have

a short operation lifetime of 2–5 years [40]. Due to insufficient stability, the propensity to darken, and the tendency to collect dust, alternatives to wax coatings are required [38].

4.1.2. Environmental Concerns

Petroleum-based waxes have a carbon footprint inherently due to their production [47]. Although little information was found in the literature regarding the photodegradation of waxes, a study from 1992 found that the biodegradation of waxes, both beeswax and paraffin, was rapid. In the study, the biodegradation rate of the waxes was monitored using a CO₂ evolution test after exposure to contaminated soil. The authors found that alkanes up to C₅₀ are completely or partially biodegradable and their decomposition products are released into the environment [48].

Biodeterioration is reportedly a problem for heritage conservation in general. It, therefore, seems probable that coating deterioration is not just a photocatalyzed process but also could be a result of biodegradation [49].

4.2. Acrylics

In the 1960s, the International Copper Research Association spearheaded efforts to find an alternative to wax for outdoor copper structures [50]. Generally, acrylics show better aging behavior than waxes, maintaining a protective function over ten years, even under aggressive artificial lighting [51]. Acrylic is an α,β -unsaturated carbonyl compound, i.e., it has both a carbon–carbon double bond and a carbon–oxygen double bond that are separated by a carbon–carbon single bond (see Figure 8). Interestingly, despite the presence of a reactive carbonyl group, based on a combination of reflection IR spectroscopy and secondary ion mass spectroscopy, no significant bonding was detected between a styrene-acrylic coating and the metal substrate [52]. Using the more interface-sensitive ATR in the Kretschmann configuration, it was found that the presence of water increases the amount of ionic bonds at the interface [53]. A more systematic study is needed to better understand the chemistry at the interface under the conditions expected for heritage conservation.

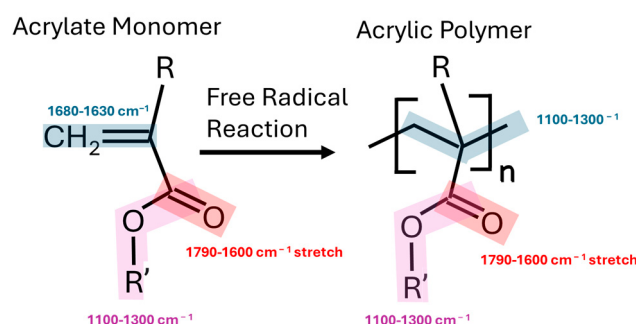


Figure 8. Schematic of both the acrylate monomer and the acrylic polymer. The regions marked for the expected IR bands are from the works of Smith and the reaction suggested by Gaytán et al. [54,55].

Since the initial work, the acrylic coating trademarked under the name “Incralac” has been widely used. In the decades that followed, numerous studies examined the performance of “Incralac” for outdoor conservation. The suitability of “Incralac” for widespread conservation of metallic heritage remains debated, however, as it is toxic [56].

4.2.1. Degradation and Challenges

Upon prolonged exposure to light, acrylics tend to weaken and undergo photo-oxidation reactions [57]. This aging is known to result in a yellowish taint. Insights into the chemical changes were gained from studies conducted on detached powder samples from museum artifacts that were pressed into KBr discs. The authors attributed the formation of a band at 1646 cm^{-1} over time to the formation of C=C bonds due to oxidation-induced unsaturation of the acrylic backbone [58]. Furthermore, the preparation process for acrylic coatings is complex, and frequently, additives are used [59]. The degradation of

the additives must also be considered when determining the suitability of acrylic coatings. For example, the IR bands associated with sodium Benzotriazole (BTA), a commonly used anti-corrosion additive, were found to disappear during aging. As a result, it was concluded that the decrease and eventual disappearance of BTA is possibly a more significant aging factor than the degradation of the actual acrylic resin material itself [58].

4.2.2. Environmental Concerns

Acrylic coatings are generally more stable than wax-based solutions, but their use is hindered by environmental concerns; specifically, the gaseous emissions of the largely hydrocarbon-based solvents are considered problematic. The EU directive 1999/13/EC calls for the protection of human health by replacing solvents in large industrial processes that are classified as carcinogenic, mutagenic, or toxic to reproduction. As a consequence, there has been a push to move towards high-solid-content coatings that use oxygenated solvents or are even solvent-free [7].

The level of emission during the coating lifetime, however, has not been determined. For the degradation studies, it seems likely that there are emissions into the environment [9]. A better understanding of emissions during the in-service degradation of the coatings is needed, e.g., what decomposition products are released during the disappearance of BTA?

4.3. Carboxylates

Carboxylates are non-toxic organic compounds that by binding to the metal surface, form a three-dimensional protective film. They can bind to the surface in different configurations that will give unique signatures in the IR spectra. See Figure 9 [60]. The wavenumbers are based on a thin film study of iron-carboxylate films measured in the transmission configuration [60].

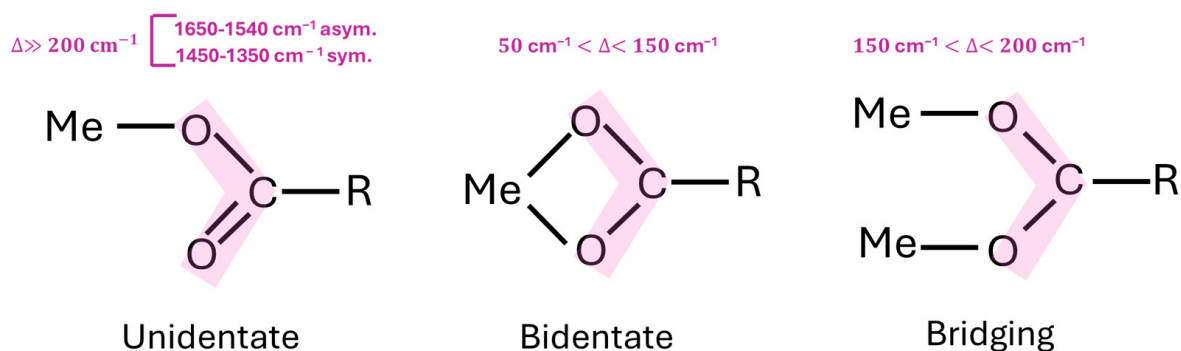


Figure 9. Schematic depicting how the carboxylates can bind to the metal surface, which would result in detectable changes in the IR spectra. The marked IR band regions are based on the work of Smith and Tanskanen et al. [60,61].

The application of carboxylates in historical conservation started in the 2000s [6]. Generally, an increase in the length of the carbon chain is considered beneficial as it results in higher hydrophobicity [62]. The performance of carboxylate coatings, however, also depends on their solubility in water (coating concentration), which decreases with the chain length [63].

4.3.1. Degradation and Challenges

The usefulness of carboxylate coatings for metals such as copper, iron, and lead has been tested. It was found that although the ability of the carboxylate to bind to the surface is central to the protective function of carboxylates, it also strongly hinders their suitability for certain metals. For lead, it was found that treatment with an aqueous carboxylate solution resulted in passivation of the surface by both the formation of lead oxide and lead carboxylate [64]. In the case of copper, however, treatment with carboxylates did not always yield ideal results. Frequent aesthetic changes, e.g., the formation of a green–blue layer due

to Cu^{2+} ions and insufficient corrosion inhibition were reported. Nonetheless, significant hydrophobicity was attained using ethanol-based solutions of myristic (tetradecanoic) acid [65]. Developing an optimized carboxylate solution requires a thorough understanding of the coating chemistry and the interaction with the underlying metal surface. A systematic study using in-situ ATR in the Kretschmann configuration could provide insights into how different formulations influence the chemistry at the metal–coating interface.

4.3.2. Environmental Concerns

The carboxylic acids used for creating the passivation layers are not considered to represent a significant environmental risk. As reiterated in the previous subsection, the main issue with carboxylates is that they do not provide sufficient protection for certain metals [66].

4.4. Polyurethane

From a chemical perspective, the main components of polyurethanes are polyols (alcohols with more than one OH group) and di- or polyisocyanates (functional group NCO). These two functional groups bind during an exothermic reaction to form extended chains and networks bonded by urethane links ($-\text{O}(\text{CO}) (\text{NH})-$). See Figure 10 [67].

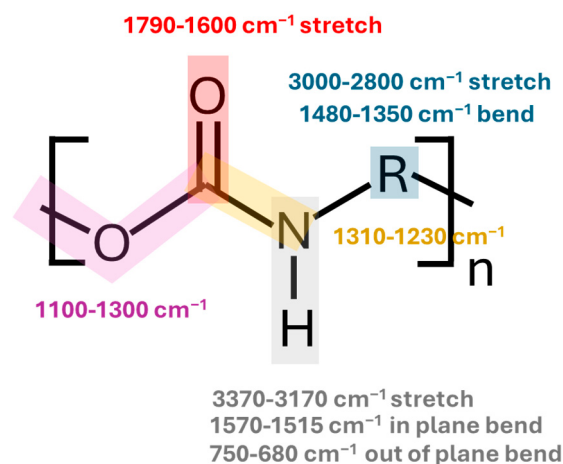


Figure 10. Schematic of the general formula for polyurethanes. The highlighted band regions are based on the work of Smith [68].

Through chemical substitution, different polyurethanes with varying properties can be attained. For example, an elastic polyurethane material is achieved by using a large polyol with a linear structure. A more rigid material is generated if a low-weight polyol with aromatic groups is used [69]. Additionally, by using a precursor with multiple isocyanate groups, a higher degree of cross-linking can be attained, which results in increased rigidity.

4.4.1. Degradation and Challenges

The photo-degradation of polyurethanes in outdoor applications leads to a reduction in molecular weight, lower tensile strength, and discoloration [70]. The degradation mechanism of polyurethanes is complex and involves many different possible reactions. In the 1980s and 1990s, the degradation of polyurethanes was widely studied using transmission IR spectroscopy of artificially aged thin samples [24]. Generally, it was found that irradiation with long wavelengths ($\gamma > 300 \text{ nm}$) resulted in oxidation of the carbon atom next to the NH of a urethane group. This resulted in a selective loss of the intensity of methylene groups at 2940 and 2860 cm^{-1} [24]. The interaction with shorter wavelengths was found to significantly depend on the chemical composition. For example, in polyurethanes based on aromatic di-isocyanates, it is widely believed that loss of aromaticity due to oxidative degradation is responsible for the color change [24].

The results attained using photoacoustic IR were compared to those attained using ex-situ ATR. Using both configurations, the same chemical changes were detected in the coatings applied to rubber samples. The changes as a result of degradation were more pronounced in the ATR spectra. The authors argue that as a greater sample thickness is probed using the photoacoustic configuration; this result indicates that the degradation is greatest in the top few microns and progresses more slowly in the regions below. This finding highlights the usefulness of coupling multiple IR configurations [71].

4.4.2. Environmental Concerns

Many of the precursors used in the preparation of polyurethanes are derived from petroleum resources. In addition to increased concerns about sustainability, there are concerns about the toxicity of precursors and polyurethanes [70]. Historically, the emission during the in-service periods of the polyurethanes was considered more or less negligible when compared to the environmental concerns associated with manufacturing and coating application [72–74].

Nonetheless, it has been found that the generated short-polymer chains, monomers, and low-molecular-weight photo-oxidized products partition into the surrounding environment [74].

4.5. Fluorinated Polymers

Per- and polyfluoroalkyl substances (PFASs) are organic polymers that contain fluorine atoms bonded to carbon. Perfluorinated and partially fluorinated are the two types of fluorinated polymers. The difference between the two is that perfluorinated polymers contain only C-F and C-C bonds, while partially fluorinated polymers contain hydrogen or other atoms besides fluorine and carbon [75]. In addition to polyvinylidene fluoride (PVDF), which is mostly applied in metallic heritage, other commonly used fluorinated polymers like polytetrafluoroethylene (PTFE) and polyvinyl fluoride (PVF) exist. PVDF is widely used because it is chemically inert and resistant to UV radiation [76]. The chemical structures of PVDF, PTFE, and PVF are shown in Figure 11.

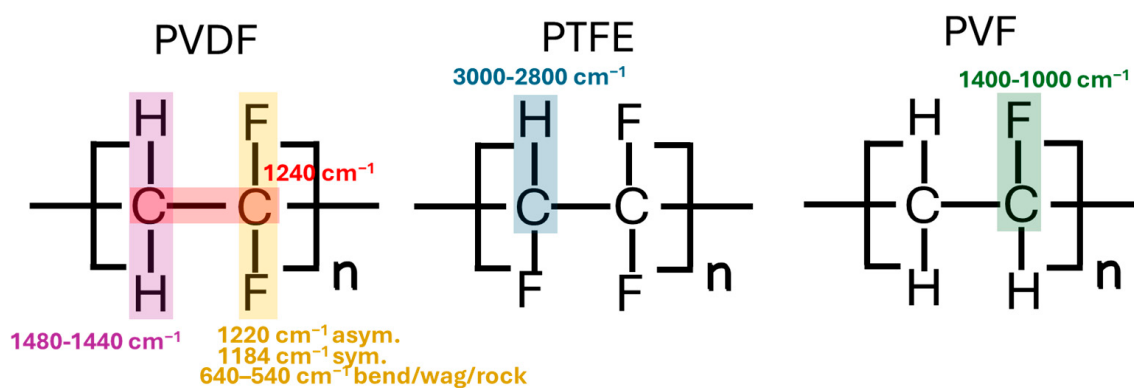


Figure 11. Schematic of the structure of common fluoropolymers. The IR band regions are based on the work of Nallasamy et al. and Bhullar et al. [77,78].

4.5.1. Degradation and Challenges

In the 1980s, some of the first applications of fluoropolymer coatings were for industrial structures, e.g., oil tanks [79]. The coatings have been found to show good stability over 20 years of service in harsh marine environments. As a result, the use of fluoropolymer coatings has significantly increased in the last decade. The global fluoropolymer coating market size was valued at around USD 300 million in 2021 [80].

4.5.2. Environmental Concerns

Beyond being widely implemented in coatings, PFASs have also found application in a wide array of consumer products, e.g., cookware and cosmetics [81]. Recently, concerns

surrounding the widespread use of PFASs and their persistence in the environment (increasing levels of contamination in the air, water, and soil) have increased. The stability of PFASs also facilitates bioaccumulation. Among others, exposure to PFASs has been associated with decreased fertility, increased risk of cancers, and lower immune system functionality [82].

The highest level of PFAS emissions is thought to occur during the manufacturing process [83]. As a result, the release of PFASs into the environment from in-service coating degradation has not been thoroughly considered. Fluoropolymer coatings are made from monomers that undergo polymerization during synthesis. Incomplete polymerization results in residual levels of monomers and smaller polymer units that could be more readily released during further processing steps or during operation [84]. A database of quantitative infrared spectra for volatile fluorocarbon gases that could be emitted from PFASs has been compiled. Using this information in combination with in-situ IR transmission studies (Figure 3c), a better understanding of the environmental impact of fluorinated polymer coatings could be gained [85]. This understanding is particularly important as both the USA and the EU are considering wide-reaching bans on PFASs due to health and environmental considerations [86].

4.6. Polysilicones

A promising alternative coating material is polysilicone [59,87,88] “Siloxane” and “silicone”, are both used interchangeably in the literature to describe compounds predominantly made of $-\text{Si}(\text{CH}_3)_2-\text{O}-$ units [89]. Silicone-based coatings should be more durable than traditional organic materials due to their silicon–oxygen bonds. The Si–O bond (bond dissociation energy 110 kcal/mol) is stronger than the carbon–carbon (83 kcal/mol) bond, i.e., it should be more resistive to oxidative degradation caused by UV radiation in the presence of water and oxygen [90].

Polysilicones are used in metal conservation because of their good adhesion to both metal surfaces and patinas [91]. They thoroughly cover many types of surfaces. They are also transparent and hydrophobic [59]. They covalently bind to the metal surface through metal–silicone interactions by hydrolysis ($\text{Me}-\text{O}-\text{Si}$), where Me is a metal surface site. Additionally, they are bonded to the neighboring molecules through siloxane bonding ($\text{Si}-\text{O}-\text{Si}$). See Figure 12 [92].

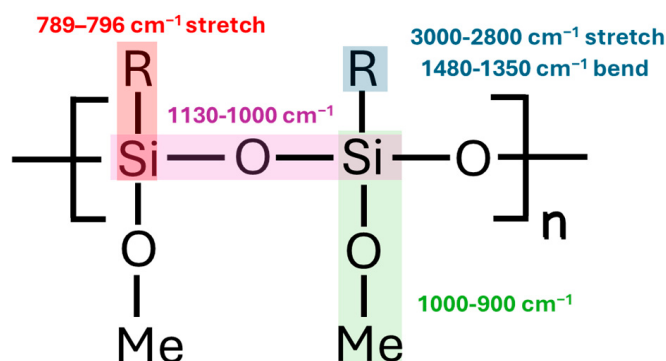


Figure 12. Schematic of the general chemical formula for polysilicone coatings bound to the metal surface. The IR band regions are based on the work of Hofmann and Al-Saadi et al. [93,94].

4.6.1. Degradation and Challenges

Short-chained silicones are less stable and more volatile than larger cyclic systems [95]. It is widely believed that the mechanism of silicone photodegradation involves the cleavage of the Si–C and the subsequent oxidation via a radical-mediated path [95]. The polysilicone chains are then likely shortened via the backbiting mechanism (see Figure 13) [96]. During the thermal decomposition of polysilicon, the release of small oligomers into the atmosphere was analyzed using gas-phase transmission IR spectroscopy [97].

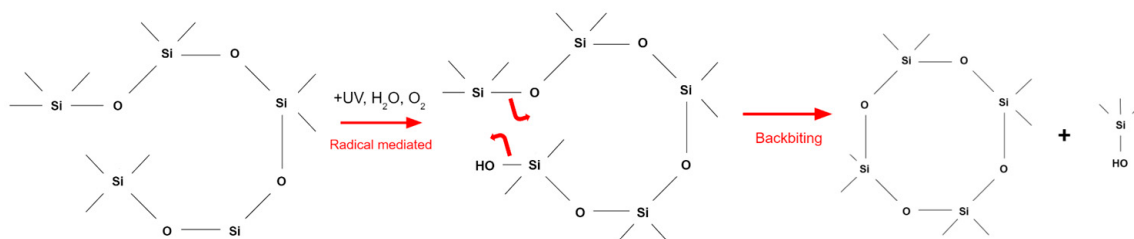


Figure 13. Simplified schematic of polysilicone photo-degradation.

4.6.2. Environmental Concerns

Beyond being considered promising for technical coatings, siloxanes are already widely used in numerous other applications, e.g., personal care products, sealants, and even food additives [98]. However, recent concerns about bioaccumulation, toxicity, and environmental hazards have been raised and now siloxanes are also considered an emerging pollutant class [98]. Despite their apparent stability, their widespread use has resulted in increased anthropogenic siloxane pollution [98,99]. The European Union, therefore, recently restricted the use of cyclic siloxanes in cosmetic products [86]. The delayed concern about the release of silicones into the environment is in part due to the lack of analytical data. To proactively avoid a similar situation of future uncertainty as that surrounding PFASs, an understanding of polysilicone coating stability and their overall environmental impact is needed. Clever implementation of IR spectroscopy in different configurations could allow not only the degradation of the coating to be studied but could also provide information about any gaseous emissions during aging. Specifically, the use of gas-phase transmission mode, photoacoustic IR, and DRIFT spectroscopy to gain temporally resolved insights into the photodegradation of industrial heritage coatings would allow for more efficient optimization.

5. Outlook

As we move away from heavy industry due to environmental concerns, many large structures with significant metallic components will be abandoned. Conservation and repurposing is an attractive alternative to the tedious dismantling of these structures. For this, however, novel anti-corrosion coatings will be needed. Many of the coatings previously used for conservation are ill suited as they lack the necessary stability against photo-oxidation or are marred by environmental concerns. In order to accelerate the development of suitable coatings, a better understanding of the degradation mechanism and information about what components are released into the atmosphere is needed.

The stability of coatings is usually determined by comparing fresh samples to those aged either naturally or in large UV chambers. The main issues with this method of study are the lack of time-resolved information and the limited flexibility, as all samples must be aged under the same atmosphere. In-situ analysis methods would enable more efficient large-scale testing of many samples under different conditions. Here we summarized different configurations of IR spectroscopy that could be applied in-situ to gain temporally resolved information about coating degradation. Using an atmospheric chamber that allows for UV irradiation, information about the gas-phase emissions could be gained from IR spectroscopy applied in the transmission configuration. By using ATR spectroscopy in the Kretschman configuration, information about changes in the chemistry at the metal-coating interface could be gained during aging. Using in-situ photoacoustic IR, depth-resolved information about variations in the coating over time could be gained, while highly surface-specific information could be probed with DRIFT spectroscopy. We predict IR spectroscopy will play an essential role in the development of novel anti-corrosion coatings for metal industrial heritage coatings.

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