



Forensic aspects of the weathering and ageing of spray paints



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ABSTRACT

This paper presents a preliminary study on the degradation of spray paint samples, illustrated by Optical, FTIR and Raman measurements. As opposed to automotive paints which are specifically designed for improved outdoor exposure and protected using hindered amine light absorbers (HALS) and ultra-violet absorbers (UVA), the spray paints on their side are much simpler in composition and very likely to suffer more from joint effects of solar radiation, temperature and humidity. Six different spray paint were exposed to outdoor UV-radiation for a total period of three months and both FTIR and Raman measurements were taken systematically during this time. These results were later compared to an artificial degradation using a climate chamber. For infrared spectroscopy, degradation curves were plotted using the photo-oxidation index (POI), and could be successfully approximated with a logarithmic fitting ($R^2 > 0.8$). The degradation can appear after the first few days of exposure and be important until 2 months, where it stabilizes and follow a more linear trend afterwards. One advantage is that the degradation products appeared almost exclusively at the far end ($\sim 3000 \text{ cm}^{-1}$) of mid-infrared spectra, and that the fingerprint region of the spectra remained stable over the studied period of time. Raman results suggest that the pigments on the other side, are much more stable and have not shown any sign of degradation over the time of this study. Considering the forensic implications of this environmental degradation, care should be taken when comparing samples if weathering is an option (e.g. an exposed graffiti compared to the paint from a fresh spray paint can). Degradation issues should be kept in mind as they may induce significant differences between paint samples of common origin.

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1. Introduction

The study of paint degradation and paint weathering is of particular interest to forensic science. Every coating material, albeit providing some optical properties such as color, luminosity and brightness, is mostly designed to protect the substrate from environmental conditions. Yet this external environment can be particularly harsh when combined heat, moisture and solar radiation act at the same time. The chemical modifications, scission of chemical bonds, or creation of crosslinkings all provide significant changes in the molecular structure of the film. As mentioned by Adamsons [1], “the chemical effects can be quickly identified at early stages of degradation using surface/near-surface analytical measurements in order to establish photo-oxidative transformation of flexible chain segments into more rigid structures, cross-link type or density changes, and/or formation of hydrophilic groups capable of adsorbing more water”. The

outcomes for the painted layer can be opticals such as color fading, mechanicals with crackings, delamination or peelings, but also chemicals and directly influent on the results of instrumental analyses. For this purpose many different analytical techniques were applied to all kind of polymers for characterizing this eventual degradation.

Among the forensic community, the majority of published papers about paint degradation concentrated on automotive coatings. The study of multi-layered original equipment manufacturer (OEM) allows chemical changes to be detected based on appearance changes, and be used to predict resistance and other time-to-failure considerations [2]. The clearcoat is obviously the most affected layer in automotive paint systems, because it is (when present) the only one in direct contact with the environment. The majority of automotive clearcoats are based on acrylic-melamine polymers and various articles concentrated on this particular composition, either analyzed by Pyrolysis GC-MS, FTIR or UV-vis spectroscopy [3–5]. Color fading, delamination of the basecoat-clearcoat layers system (either adhesive or cohesive failures [1]), and the paint mechanical deterioration were also deeply investigated [4,6,7]. Most of these studies involved surface or near-surface analyses mostly carried out by attenuated

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total reflectance infrared spectroscopies (ATR-IR). As the degradation penetration depth is time-correlated, the surface will always present the most important modifications.

To increase stability over time the industries have developed solutions for protecting the painted film. Ultraviolet Absorber (UVA) and Hindered Amines Light Absorbers (HALS) were both used to absorb the excess of photons and avoid their associated energy to be used for breaking the chemical bonds [6,8–10]. These were proved very useful in various situations and drastic increase of the stability can be reached [11,12].

The second main field to have been investigated deeply for paint degradation is the artistic and cultural heritage. One particularity of ancient artistic paintings is the potential use of proteinaceous binders, for which the degradation has been studied with the objective to be able to predict their long-term behavior [13]. Others have compared synthetic binders such as polyvinyl acetate and acrylic [14], or acrylic and alkyd paints [15,16]. Different binders were studied by Papiaka and coworkers, who demonstrated that the risks of chemical modification due to UV exposure are superior to both heat and humidity factors [17].

Finally the domestic paints encountered in forensic cases have not been studied much because the problems of degradation associated were not as essential as in the industry or in the conservation fields. From the forensic point-of-view however, it might be decisive to prove that a degradation has occurred. Demonstrating that specific photo-oxidation products appeared in the paint film is necessary when unexplained spectral differences are to be used as evidence of uncommon origin. Trace materials have acquired characteristics, and it is crucial to be able to infer an explanation for these differences. Concerning the domestic paints, the use of UVA or HALS is also less likely as in most cases they are cheaper to produce and not necessarily designed for extended outdoor exposure. The different binders used also reflect this predominance of cheaper materials. Recent studies on spray paints have shown that a vast majority of the binders were based on alkyd modified polyesters (orthophthalic and isophthalic acids mostly) [18]. These binders do not have the same properties as acrylic monomers and do not react similarly under strong UV-light exposure. The main modifications in infrared spectra of acrylic paints were pointed out to be a decrease and broadening of the

carbonyl peak at around 1730 cm^{-1} [15,19], and also around $2800\text{--}3400\text{ cm}^{-1}$ for which the methylenic, hydroxy, amine and carboxylic acid envelopes are present. Alkyd paints on the other side were shown to be mostly affected around the same $2800\text{--}3400\text{ cm}^{-1}$ region [5]. This area, as pointed out by Adamsons [2], is particularly interesting for quantifying the degree of degradation and the accumulation of oxidized products, as the ratio of the two envelopes increases with UV exposure. The so-called photo-oxidation index (POI) is calculated as follow, based on data previously normalized to the methylenic --CH_2 stretch at 2930 cm^{-1} and baseline corrected (Fig. 1):

$$\text{POI}_\Delta = \frac{[\text{OH, NH, COOH}]}{[\text{CH}]} \quad (1)$$

As most of the spray paints are based on alkyd polyesters binders [18], it is therefore necessary to better understand their chemistry in order to predict the eventual degradation and the consequences on subsequent instrumental analyses. The various binders, pigments and/or extenders do not have the same stability in regard to solar radiation or moisture, as are the different kinds of paints (artistic, domestic or automotive).

The following sections will present some theoretical aspects of the paint degradation. It is followed by an example of application using a sample set of 6 spray paints, measured systematically after days/weeks/months, and left to degrade for a total period of 3 months. These results are later compared to an artificial weathering using a climate chamber. Both photo-oxidation indexes and PCAs are used to evaluate the results and estimate the degree of degradation observed on these samples.

2. Theory on paint degradation

Solar radiation is often considered the main and most important factor of the paint degradation. In fact, it is the UV portion of the electromagnetic spectrum that is mostly responsible for the degradation (UV-A, UV-B and UV-C). These short wavelengths and highly energetic radiations possess photons sufficiently energetic to catalyze and supply the photo-oxidation process in the presence of oxygen. Different mechanisms of the chain photo-oxidation process for polymers were described in the literature [20,21].

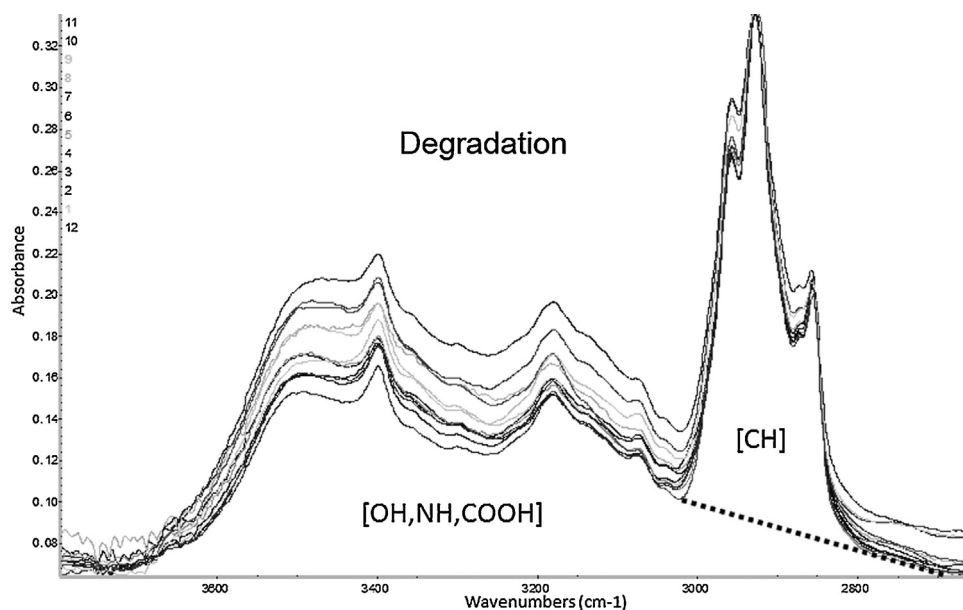


Fig. 1. Illustration of photo-oxidation index calculation, using the two envelopes of the methylenic (CH), and hydroxy, amine and carboxylic acid (OH, NH, COOH). Spectra are normalized to the methylenic --CH_2 stretch ($\sim 2950\text{ cm}^{-1}$) and one can observe an increase of oxidized products over the radiation received.

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