TU Delft

Delft University of Technology

Determination of early warning signs for photocatalytic degradation of titanium white oil paints by means of surface analysis

van Driel, B. A.; Wezendonk, T. A.; van den Berg, K. J.; Kooyman, P. J.; Gascon, J.; Dik, J.

DOI
10.1016/j.saa.2016.04.026

Publication date
2017

Document Version
Accepted author manuscript

Published in
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

Citation (APA)
van Driel, B. A., Wezendonk, T. A., van den Berg, K. J., Kooyman, P. J., Gascon, J., & Dik, J. (2017). Determination of early warning signs for photocatalytic degradation of titanium white oil paints by means of surface analysis. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *172*, 100-108. https://doi.org/10.1016/j.saa.2016.04.026

Important note
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Copyright
Other than for strictly personal use, it is not permitted to download, forward or distribute the text or part of it, without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license such as Creative Commons.

Takedown policy
Please contact us and provide details if you believe this document breaches copyrights.
We will remove access to the work immediately and investigate your claim.

This work is downloaded from Delft University of Technology.
For technical reasons the number of authors shown on this cover page is limited to a maximum of 10.

© 2017 This manuscript version is made available under the CC-BY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/
http://dx.doi.org/10.1016/j.saa.2016.04.026
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, vol. 172, 2017
Driel, B.A. van, Wezendonk, T.A., Berg, K.J. van den, Kooyman, P.J., Gascon, J., Dik, J.
Determination of early warning signs for photocatalytic degradation of titanium white oil paints by means of surface analysis.

Supplementary information

In the current paper, we follow the aging of unvarnished titanium white oil paints on the nano-scale with AFM and XPS and we relate this to the macro-scale phenomena of gloss change and chalking. The supplementary information contains parts of the paper that relate to the images in the SI.

"In practice, an oil paint film has a so-called medium skin (see Fig. S1[3]), which is a thin layer of unpigmented oil at the surface of the paint film formed during the drying process. The thickness of this layer (t_{ms}) depends on, among others, pigment volume concentration (PVC) and manner of application[39]."

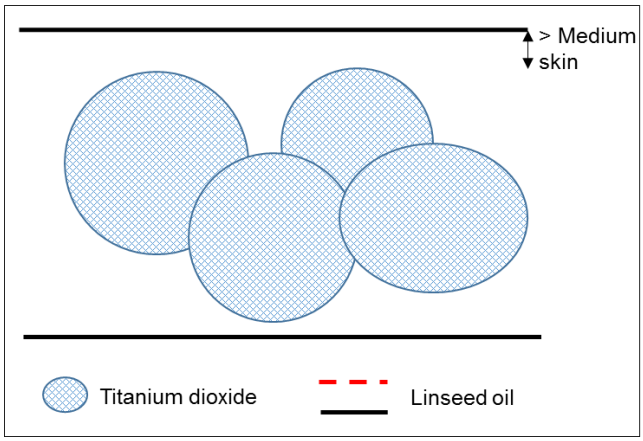

Figure S1: Schematic representation of an unaged paint film with its skin of medium

"After drying, the paints were cut into seven fragments of 1 by 2 cm and one larger fragment of 7.5 by 2.5 cm, Fig. S2. The larger fragment was used to monitor gloss during the aging process. After the gloss measurement, the large sample was returned to the aging chamber. The small fragments were taken out of the UV chamber at different irradiation dose and were analyzed using XPS and AFM on multiple spots."

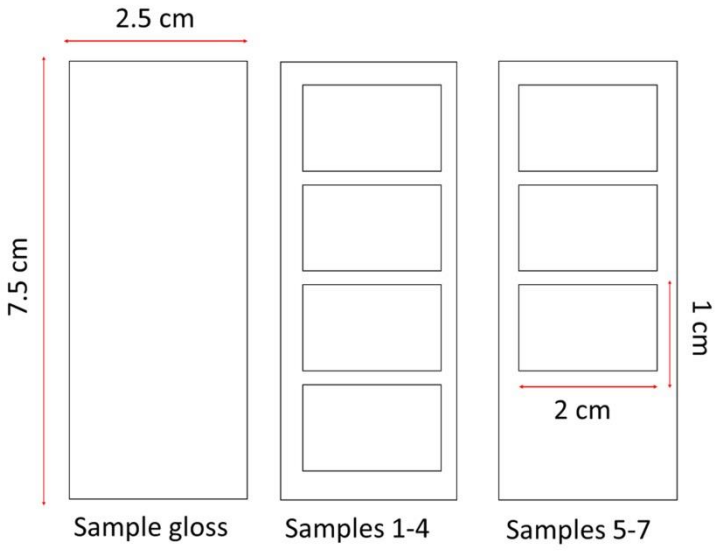

Figure S2: Scheme of sample preparation.

*"AFM analysis was performed using an NT-MDT Ntegra instrument equipped with a silicon Etalon tip. Samples were analyzed at three to five different locations of either 10 * 10μm or 20 * 20 μm. In case*

of visible sample heterogeneity (Figs. S3 and S4), clearly distinct areas (white and yellow) were both analyzed in three to five locations.

…..

As expected, inhomogeneity of aging was observed. Intermediate samples of UA-1 (I_4-I_6) had clearly visible yellow and white areas, (Figs. S3a and S4). In this case, the white and yellow areas were analyzed separately labeled 'via yellow' and 'via white' respectively. In gloss measurements, the inhomogeneity is averaged out due to the large measuring area. The difference in color is a result of the various stages in the degradation process. In white areas, the oil binder had decomposed, and consequently it did not produce a yellow color. In the white areas, degradation is visible by eye. Yellow areas were still visibly in an earlier degradation stage and had not started chalking [43]. In yellow areas, degradation is not visible by eye yet. Therefore 'via yellow' is of more interest for the determination of early warning signs.

…..

UA-1 line scan locations were oriented on white or yellow areas by using the built-in sample microscope, whereas for the UA-2 and CR samples random locations on the overall yellow paint film were studied (Fig. S3)[1]*.*

…..

The inhomogeneity of the UA-2 samples was far less pronounced (Fig. S3c). The paint film seemed to degrade more gradually and remained yellow until it had reached the point of severe chalking. Therefore, results of UA-2 are not differentiated in yellow and white[1]*. As anticipated, the CR samples showed no signs of degradation (Fig. S3b), and are treated similarly to UA-2."*

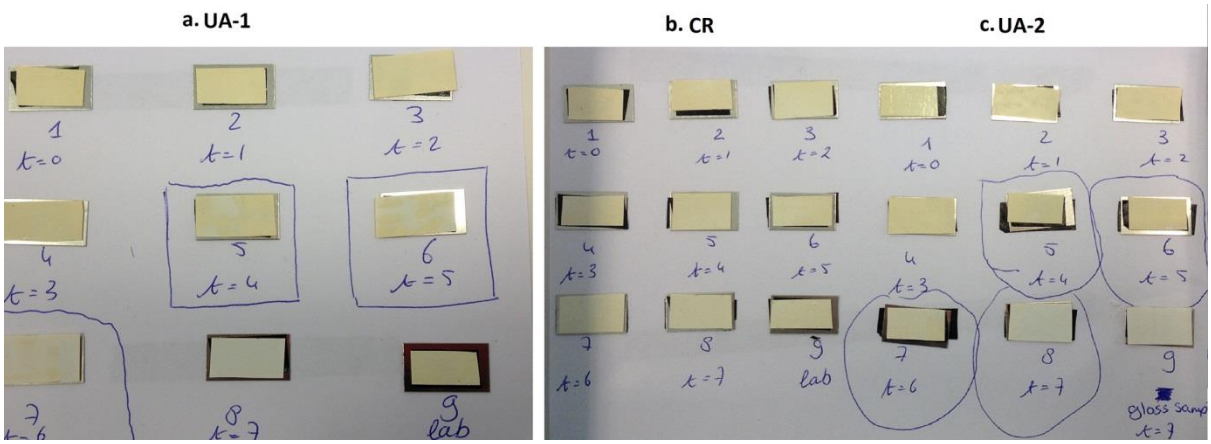

Figure S3: Samples for XPS: a) UA-1, b) CR, c) UA-2

Figure S4: Example of an intermediate inhomogeneous sample with white (chalked) and yellow (yellowed oil due to dark storage) areas. The contrast is enhanced to increase visibility.

[1] XPS

"The photostable reference (CR), illustrated in Figs. S5 and Fig. 3, shows high stability in the height difference during irradiation. The same holds for the sample kept in the lab environment as illustrated in Fig. S6."

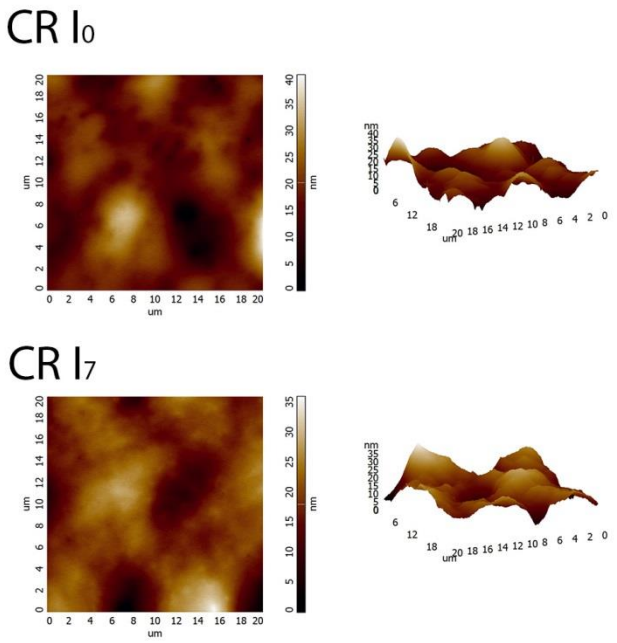

Figure S5: AFM images of CR samples I_0 and I_7

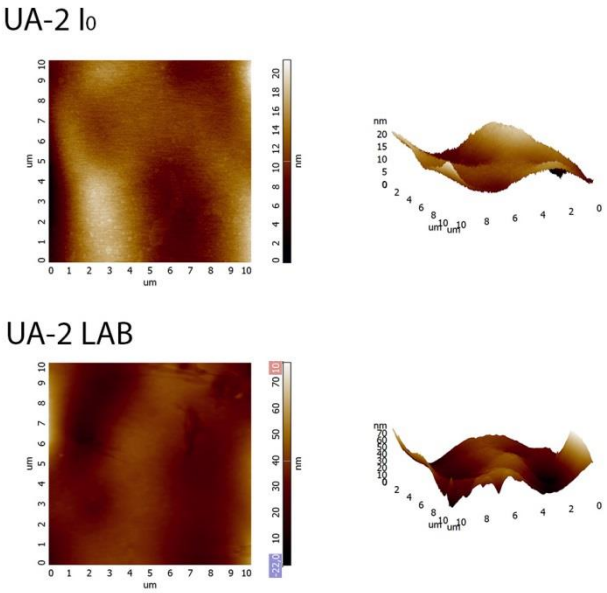

Figure S6: AFM images of UA-2 samples I_0 and LAB

"XPS survey spectra of UA-1 are shown in Fig. 4a; the total survey spectrum is shown in Fig. S7a. The observed signals in the survey spectra are identified as C1s (284.8 eV), Ti2p (485.8 eV) and O1s (532.4 eV). In the initial I_0 sample, only carbon and oxygen signals are present. This remains the case in samples I_2 and I_3: after >5200 J/cm^2 of irradiation, there is no clear signal for titanium. The spectra for I_4 differ from the previous ones: a clear Ti contribution can be distinguished around 458.8

eV. The specific binding energies of the Ti2$p_{3/2}$ (458.8 eV) and Ti2$p_{1/2}$ (464.5 eV) signals confirm the oxidized nature of the titanium species. The Ti peak intensity is further enhanced for samples I_5 to I_7, indicating that increasing amounts of TiO_2 are located on the surface of the paint.

….

Core-level spectra of carbon are displayed in Fig. S7b."

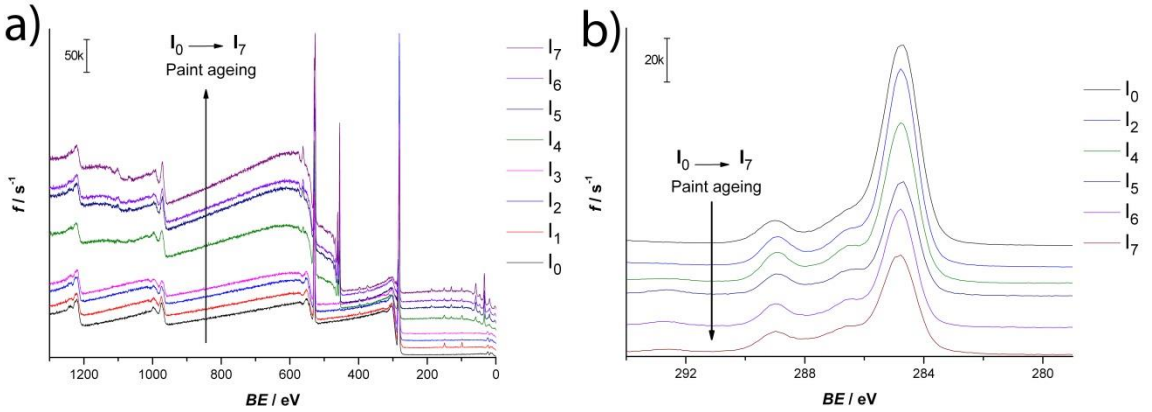

Figure S7: a) UA-1 XPS total survey spectra and b) C1s core-level spectra.

"To investigate the degradation of the paint in more detail, UA-2 paint films were analyzed with XPS, since the overall yellow paint film seemed to degrade more gradually and homogenously. Survey spectra of UA-2 samples are displayed in Fig. 6a (total survey in Fig. S8) with the relative atomic composition in Fig. 6b."

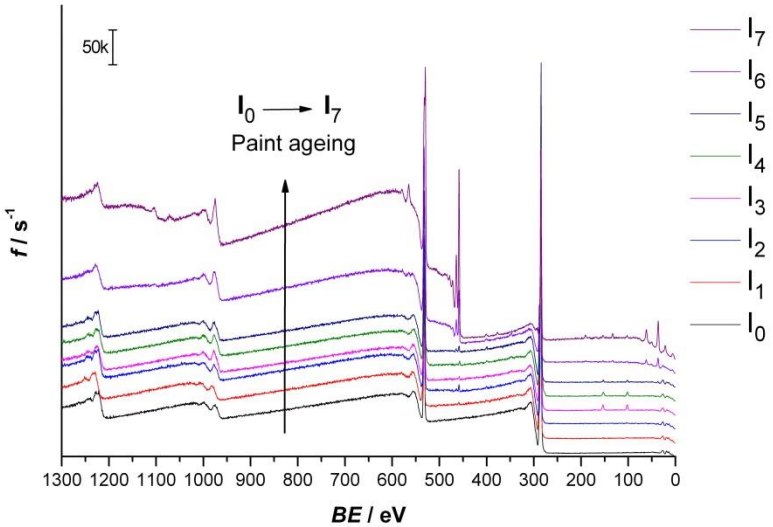

Figure S8: UA-2 total survey spectrum.

"XPS analysis of CR shows high stability of the survey spectrum during irradiation (Fig. S9). The characteristic Ti contribution is not detected in any of the spectra. The same is true for samples aged under lab conditions."

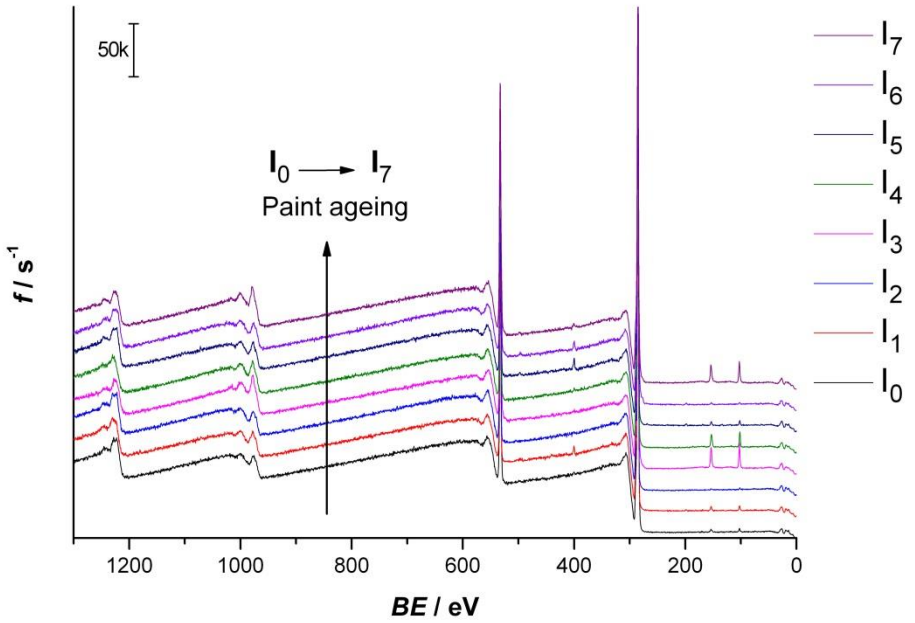

Figure S9: CR total survey spectrum.

Note on XPS survey spectra

In some spectra, traces of a Si phase are observed, as very minor Si2s (151 eV) and Si2p (99 eV) signals are present (Figure S7 - S9). However, atomic contribution is below 1%. Similarly, traces of a N phase are observed, as minute signals of N1s (398 eV) are present in some samples.