Diffusion-Controlled Staining and Degradation of Organic Coatings

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INTRODUCTION

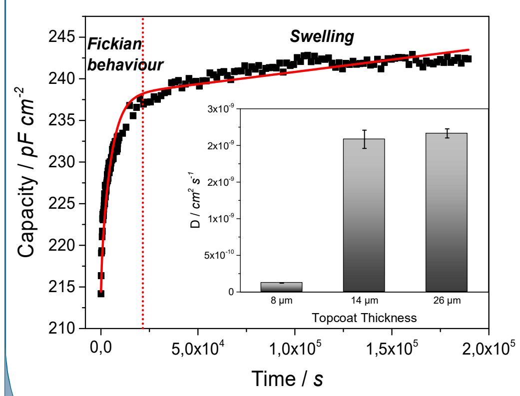
Staining as well as chemical degradation of organic coatings is frequently induced by diffusion of aqueous and nonaqueous transport media into the coating. This process is followed by softening of the polymer film and a further transport of critical molecules into the polymer. In this work several complementary techniques are employed to analyse these transport processes in a white thermoset PU coating with a dry film thickness of 25 µm on HDG steel.

EXPERIMENTAL

Water-Uptake & Electrochemical Degradation

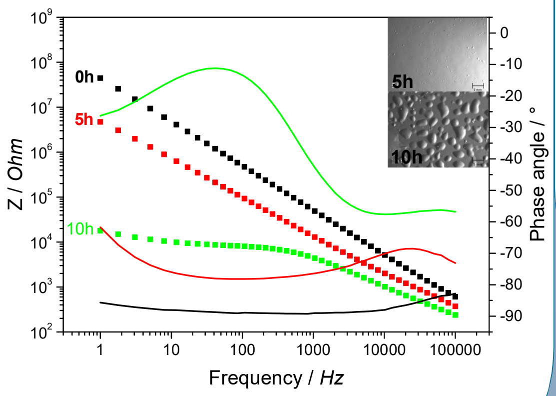
- Two-Stage diffusion process in water (Borate Puffer, pH = 8,5):
  1. Fickian behaviour (0-30 min)
  2. Non-Fickian „Swelling" (>30 min)
- Diffusion coefficients of stage 1 at room temperature are typically in the range of 10^{-9} cm^2 s^{-1}.
- D in stage 1 exhibits pronounced dependence on the coating thickness.
- A total water uptake of 2-4% was calculated according to Brusher-Kingsbury [1].
- Long-term degradation in saline environments can be enhanced with elevated temperatures [2].

Initial State (Borat Puffer)



EIS measurements show changes in capacity in the initial state. Diffusion coefficients can be calculated [1].

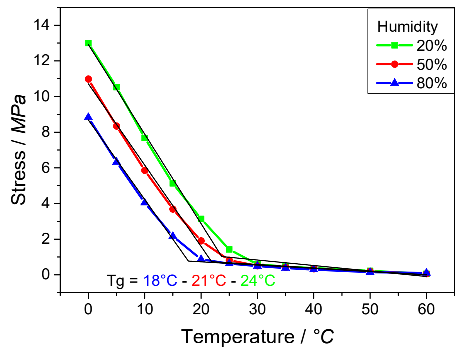
Long-term Degradation (Na_2SO_4)



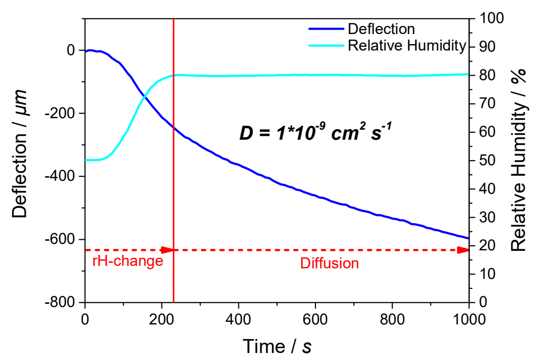
Bode-Plot gives information about corrosion behaviour starting with blistering [2].

Tg-Reduction - Stress Relaxation

- Changes in relative humidity are reflected in coating properties as well: An increase from 20 → 80% r.H. results in Tg-Reduction of 6°C.
- In parallel a reduction of intrinsic Stress in the coating is observed. According to [3] intrinsic stress in coatings contributes to blistering.
- Fitting a Fickian diffusion process to stress relaxation data (in the range of steady r.H.) results in diffusion constants comparable to the EIS results.



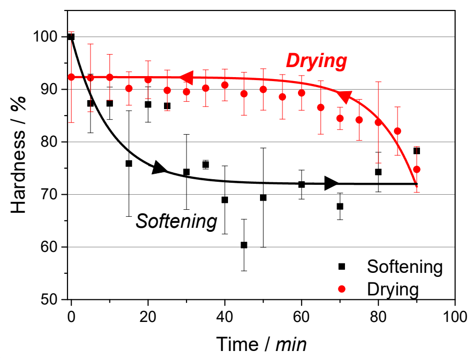
Higher humidity softens the coating and leads to lower glass transition temperatures.



Diffusion processes at 5°C initiated by r.H.-change follow Fickian diffusion law.

Coating Softening

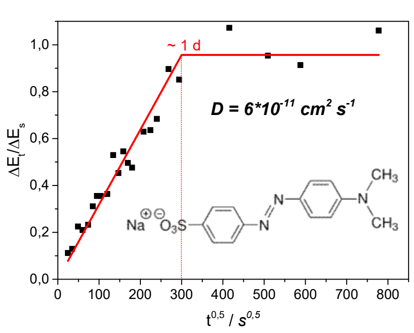
- Initial Water-Uptake is accompanied by a significant softening of the polymer: Reduction in microhardness of approximately 30%.
- This process is predominantly reversible.
- 90% of the redrying step occur within 30 min.



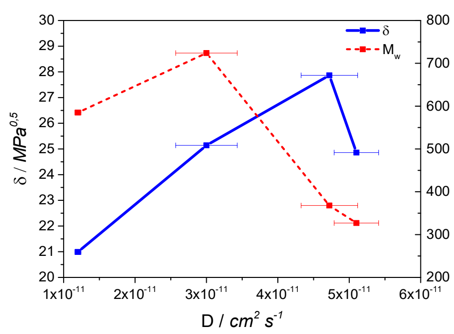
Water uptake influences microhardness of organic coatings. Before drying, samples were stored in water for 90 min.

Transport of Molecular Substances

- Dyes can be used as models for uncharged or charged higher molecular species penetrating the coating film.
- Colour (i.e. spectral reflection) measurements are suitable to quantify Fickian diffusion behaviour of dyes.
- Diffusion coefficients are found to be two orders of magnitude smaller than water and show a dependence upon the molecular weight of the species and its solubility as defined by the Hildebrandt parameter.

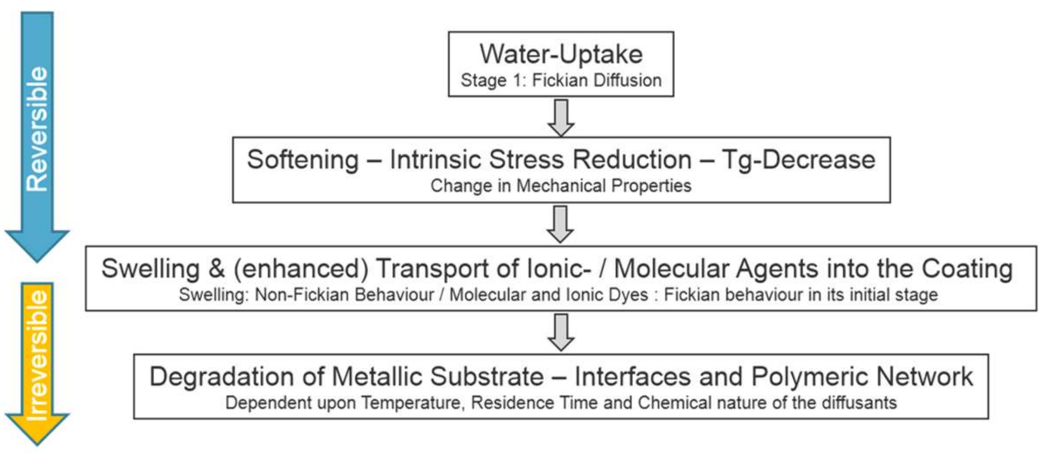


Diffusion of methyl orange shows also Fickian behaviour but resulting in lower diffusion coefficients.



Low molecular weight and high solubility result in higher diffusion coefficients.

CONCLUSION



- Initial process is usually Fickian diffusion as shown in the EIS measurements by a change in capacity.
- Softening of the coating facilitates bigger diffusants by reduction of Tg and microhardness.
- Microhardness measurements represent the reversibility of water diffusion after 90 min humidity storage.
- Water acts as a carrier for soluble species. As demonstrated by colour measurements, ionic azo dyes diffuse in the coating a hundred times slower than water depending on their molecular weight and solubility.
- Defects in coatings induce corrosion effects and starts locally as blisters which is indicated by the Bode-Plot.
- EIS and stress relaxation are comparable methods. Diffusion coefficients obtained with both techniques are found to be in the same range.

REFERENCES

[1] D. Brasher, A. Kingsbury, Electrical measurements in the study of immersed coatings on metal. I. Comparison between capacitance and gravimetric methods of estimating water uptake, *J. Appl. Chem.* **4** (**2**) (1954) 62 – 72.
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[3] T. Prosek, A. Nazarov, M.-G. Olivier, C. Vandermiers, D. Koberg, D. Thierry, The Role of Stress and Topcoat Properties in Blistering of Coil-Coated Materials, *Prog. Org. Coat.* **68** (2010) 328 – 333.