Plasticized PVC and minced mutton meat in an Artwork by Dieter Roth – challenges in understanding its aging behavior through scientific studies

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Introduction

The following study has been done as part of a Diploma-Thesis which deals with the Conservation and Restoration of the **Artwork PO^EMETRIE** (1968), by **Dieter Roth** (see fig. 1). **Scientific investigations** were carried out **to understand the aging behavior of the involved materials**, namely plasticized poly (vinyl chloride) (p-PVC) and minced mutton meat.

The object itself is a book, consisting of a p-PVC plate as book cover and transparent p-PVC bags as pages. The bags are printed from the outside, while being stuffed with minced mutton. Due to **plasticizer migration**, **fat diffusion and leakage**, **the texts floats in and on a sticky brownish surface** layer and is at massive risk of being lost.

Scientific investigations were carried out on the object for the identification-characterization of its main materials and degradation products but also on artificial accelerated thermally aged p-PVC-based models. The influence of factors such as soling, meat, and fat was considered in the p-PVC-based models, in order to understand the main mechanism of ageing. Further investigations were done on surface cleaning with a focus on the use of surfactants.

Fig. 1: PO^EMETRIE (1968), by Dieter Roth, (0,4 -7,5 x 86,5 cm x 26,3 cm H x W x D) before conservation treatments.

Experimental

Methods: Fourier transform infrared – attenuated total reflection **(FTIR-ATR)** spectroscopy and pyrolysis – gas chromatography / mass spectrometry **(Py-GC/MS)** were used to identify the object materials and assess its state of conservation but also to elucidate the testing material composition and ageing conditions.

- FTIR-ATR analysis were done using an **Alpha-p FTIR Spectrometer (Bruker)**, based on a Rock solid system with a platinum-ATR-sample modulus as diamond crystal. Spectral measurements were taken between 4000-375 cm^{-1} by 4 cm^{-1} resolution. Measurements were done with 128 scans.

- Py-GC/MS measurements were done using a **Pyrolyzer PY-2020id (Frontier Lab)** with **GCMS-QP2010 Plus (Shimadzu)**; column SLB-5ms (Supelco). GCMS Realtime® Pyrolysis (Py) T 600 °C. Interface T 250 °C; injector T 280 °C.

Pre-tests as first step: to understand the ageing behavior of the objects commercial PVC bags (Dia-Bags, PANODIA) **and plates** (JEDI Kunststoff GmbH) were selected and artificially aged under different conditions (light and thermal ageing at different temperatures and times, with and without artificial soiling and different fillings). **Immersion-tests** were also done to select the most suitable cleaning agent.

Main testing series as second step: for this part of the study the following parameters were then selected:

Soiling types:
- Soil 0: no soiling / Soil 1: carbon black and paraffin oil (95:5) / Soil 2: clarified butter and DEHP (2:1, Soil 2).

Artificial thermal ageing:
- 50 °C and 70 °C / soiled samples has been aged for two weeks.

Cleaning agents:
- Distilled Water / isopropanol / Orvus® WA Paste (5 %) / Hostapon® TPHC (5 %)
- Microfiber cloth (Evolon® CR) was used to wipe away the soilings

To study the material behavior and cleaning efficiency, **optical microscopy (OM)** and **FTIR-ATR analysis**, as well as **weighing of the samples** were carried out before soil application, after soil application, after aging and after cleaning.

For OM a Keyence VHX-6000 (RZ 100x-1000x objective - VH-Z100R) equipped with a LCD monitor and a CMOS camera (virtualpixels: 1600 (H) x 1200 (V)).

Results

Object investigations:

FTIR-ATR and Py-GC/MS were used to identify the **object materials** and to assess its state of conservation. FTIR-ATR results showed that the **transparent bags** were made of **PVC plasticized with phthalates** (fig. 2), while Py-GC/MS data indicated that the phthalates-based plasticizers in the PVC were mostly likely based on **di-(2-ethylhexyl) phthalate (DEHP)** (fig. 3). Some pyrolysis products registered for the transparent bags further suggested the **advanced state of degradation** of the DEHP.

The yellowish plate was made of **PVC plasticized** with phosphate-based flame retardants according to the FTIR-ATR results (fig. 5) and more precisely by **tricresyl phosphate (TCP)** and minor amounts of phthalates-based plasticizers (fig. 6).

Finding suitable **model sheets** proved difficult as regulations severely restrict the use of certain phthalate and phosphate plasticizers. On the other hand, transparent PVC bags with DEHP (Dia-Bags, PANODIA) (see figs. 2 and 4) and a transparent PVC plate containing triphenyl phosphate (TPP, JEDI Kunststoff GmbH) (see figs. 5 and 7) instead of TCP could be found, which were used in this study.

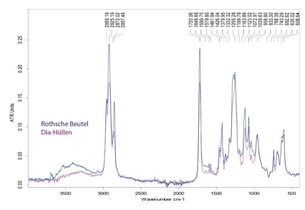

Fig. 2: FTIR-ATR comparison of the Roth-bags (blue) and the Dia-bags (purple).

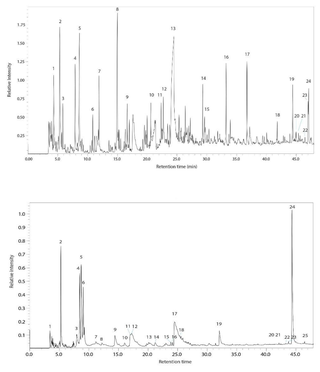

Fig. 3: Py-GC/MS analysis of the Roth-bags, Peak# 19 shows phthalic acid 2-ethylhexyl hexyl ester.
Fig. 4: Py-GC/MS analysis of the Dia-bags, Peak# 24 shows DEHP.

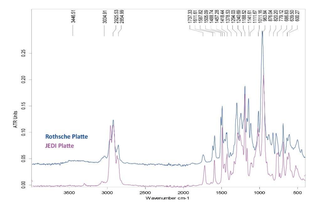

Fig. 5: FTIR-ATR comparison of the Roth-plate (blue) and the JEDI-plate (purple).

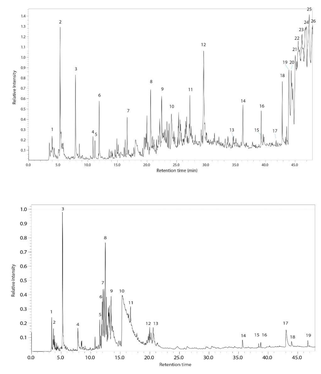

Fig. 6: Py-GC/MS analysis of the Roth-plate, Peak# 22-26 shows TCP, # 12 shows DEP, # 13-14 DiBP, # 18 phthalic acid 2-ethylhexyl hexyl ester.
Fig. 7: Py-GC/MS analysis of the JEDI-plate, Peak# 17 shows TPP.

Main testing series:

- **Optically**, a slight **colour change to yellowish or reddish** could be determined macroscopically and by OM in all samples after thermal aging (see figs. 8, 9, and 12, 13). The highest temperature of 70 °C lead to the greatest changes in colour.
- **FTIR-ATR analysis** established that the **colour change** was **due to the dehydrochlorination of PVC;** all samples showed an increase in the peaks relative intensity at 3300 (OH), 3078 (CH aromatic), 1638, and 1565 cm^{-1} (C=C) after thermal ageing (see figs. 10 and 14). Through thermal ageing no plasticizer migration could be detected, neither on the soiled or unsoiled samples.
- The **weight measurements** showed an **increase in weight after soiling** and as well as a **weight loss after ageing** and a **slight weight loss after cleaning**. While weight loss is indicating a **loss of plasticizers and volatile compounds**, only the samples soiled with Soil 2 showed an increase in weight. No to significant difference could be found in any of the cleaning agents by weight (see figs. 11 and 15).

MACROSCOPIC | OM | FTIR-ATR | WEIGHT

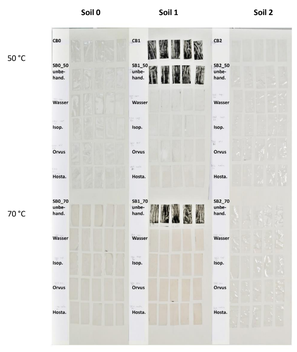

Fig. 8: cleaned Dia-bag samples.

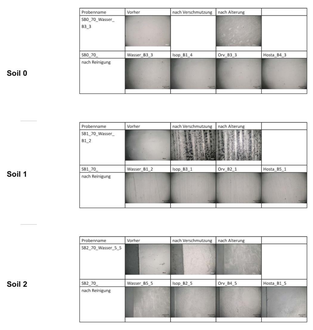

Fig. 9: OM cleaned Dia-bag sample.

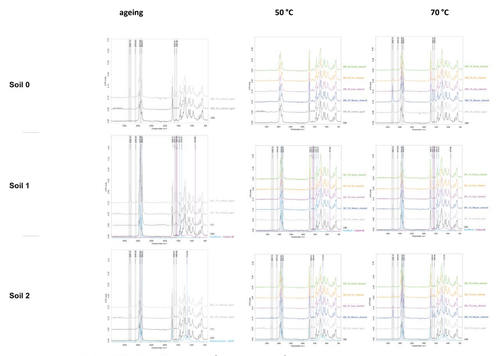

Fig. 10: FTIR-ATR analysis Dia-bags.

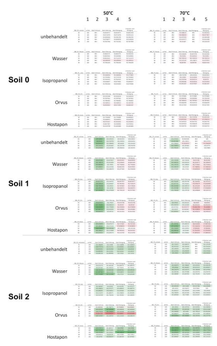

Fig. 11: Weight Dia-bags.

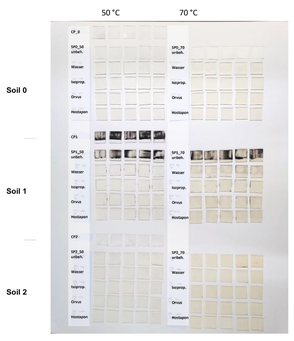

Fig. 12: cleaned JED-plate samples.

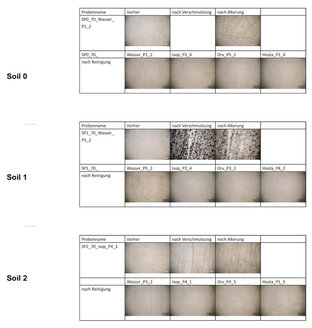

Fig. 13: OM cleaned JEDI-plate samples.

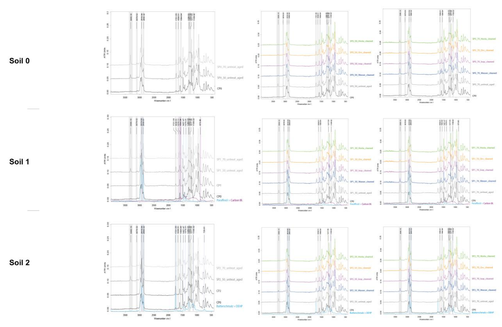

Fig. 14: FTIR-ATR analysis JEDI-plate.

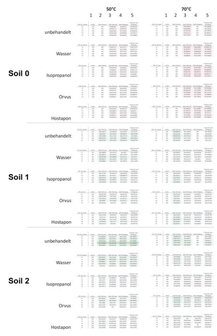

Fig. 15: Weight JEDI-plate.

- All the **cleaning agents** were able to **reduce soiling** optically and FTIR-ATR analysis confirmed a decrease in the intensity of peaks associated both with the soiling and the peaks associated to dehydrochlorination (see figs. 10 and 14 - blue or purple background and gray background, respectively). **Distilled water** showed **to poorest cleaning results, isopropanol the best ones**, while the surfactants range in the middle (could reduce soiling and dehydrochlorination, but minor residues remained on the surface).

Conclusion

- **Scientific studies** on the selected **artwork successfully identified and characterized the materials chemical composition** and its advanced **state of degradation** (plasticizer migration, fat diffusion and leakage).
- The main **PVC and phthalates** composition of the **bags** and **PVC and phosphates** of the **plate** were identified by FTIR-ATR, while the exact type of phthalates and phosphates was clarified by Py-GC/MS analyses (DEHP and TCP, respectively). The diffusion of the plasticizer towards the surface and its main state of degradation war further characterized by both methods.
- **FTIR-ATR, OM, and weight measurements** on the **selected models of PVC bags and plates** before and after the thermal ageing for the main testing series, were of **help for assessing the ageing behavior of the materials** and for **then selecting the proper cleaning agent**.