

## Appendix 3: Analysis of degradation products found during surveys of three French collections

Under exposure to light and ultra violet radiations, and under the influence of temperature, oxygen and high humidity, chemical reactions take place in plastics and lead to modification of their properties. Reactions like chain scission, cross-linking and chromophoric group formation result in loss of physical properties of the plastic and cause perceptible changes such as crazing, brittleness and discolouration. This might lead to the formation of degradation products that are released by the artefact. When surveying a collection, the most obvious phenomenon is the presence of deposits either liquid or solid on the surface of degraded objects. It corresponds to the migration of compounds added during plastic manufacturing. One also might smell some characteristic odours emitted by plastics by off-gassing of volatile organic compounds (VOCs).

Among all the works surveyed, seventeen were singled out for presenting degradation products to be analysed. The majority was in solid form, crystal or powder, and only three in liquid form. Relevant VOCs were identified in some cases.

### a. Characterisation of solid and liquid residues

The appearance of deposits on the plastic surface is generally attributed to the plasticiser migration. This change in the material structure has a consequential change in the physical property, the object becoming more brittle. But other reactions can contribute to the formation of products on the surface.

Other additives such as plasticiser and fillers that are compounded in the plastic formulation may result in surface residues. They are not always considered as degradation products, because they do not result in chemical decay, nevertheless, in the framework of survey, we did consider as a degradation product any material present on the surface and that was not attributed to dirt or dust.

Such products were collected and micro sample of plastic substrate was done to perform a deeper analytical investigation and to better characterise the polymer composition and degradation path. Solid deposits were



collected either with scalpel or tweezers while liquids were sampled with the help of a needle when drops were visible and a cotton swab in the other cases. Samples were kept in glass containers to avoid any risk of contamination. Analyses were performed following the analytical method previously implemented for the SamCo materials: an infrared spectroscopy analysis possibly followed by a Py-GCMS analysis when complementary information was necessary (see chapter 1).

Analysis reveals the presence of plasticisers in most of the cases, showing that their migration is a common phenomenon although fillers, a mineral charge added to modify physical and optical attributes, has been also identify among the residues. Plasticisers are added to obtain flexible plastics and because they are not chemically bounded to the polymer substrate they can move to the surface under appropriate conditions. Depending on its chemical nature, they appear in a solid state that can be misidentified as dust in the early stage of degradation or in liquid that makes the plastic surface sticky. Two artefacts from the musée Galliera (Paris) illustrate such degradation.

The first one is a celluloid comb (museum number 58.69.40) (Figure 1) dated around 1910, which is broken in several pieces corresponding to an advanced stage of degradation. In the internal face of the polyethylene storage bag, tiny particles having the shape of needles are visible. FTIR carried out on loose residues reveals the presence of camphor, a common plasticiser for cellulose nitrate. Chemical analysis of the solid plastic confirmed the presence of cellulose nitrate and camphor as being present in the plastic bulk and confirms the visual material identification made during survey.

The other object is a black PVC raincoat from the 1970's made by the French couturier Paco Rabanne (museum number 1972.23.2, musée Galliera, Paris) which has been moulded in one piece. It presents one of the most interesting cases of decay found during the surveys. The whole surface of the plastic is covered by a dramatic sweating in the form of large drops of a yellowish and sticky substance which make the coat quite impossible neither to handle nor to store (Figure 2). It is laid on a cotton cloth protected by polyester sheets inside



**Figure 1.** Comb, ca. 1910 example of a celluloid object (Cellulose nitrate plasticised with camphor) at its final step of degradation (© C2RMF, photo Thomas Clot)



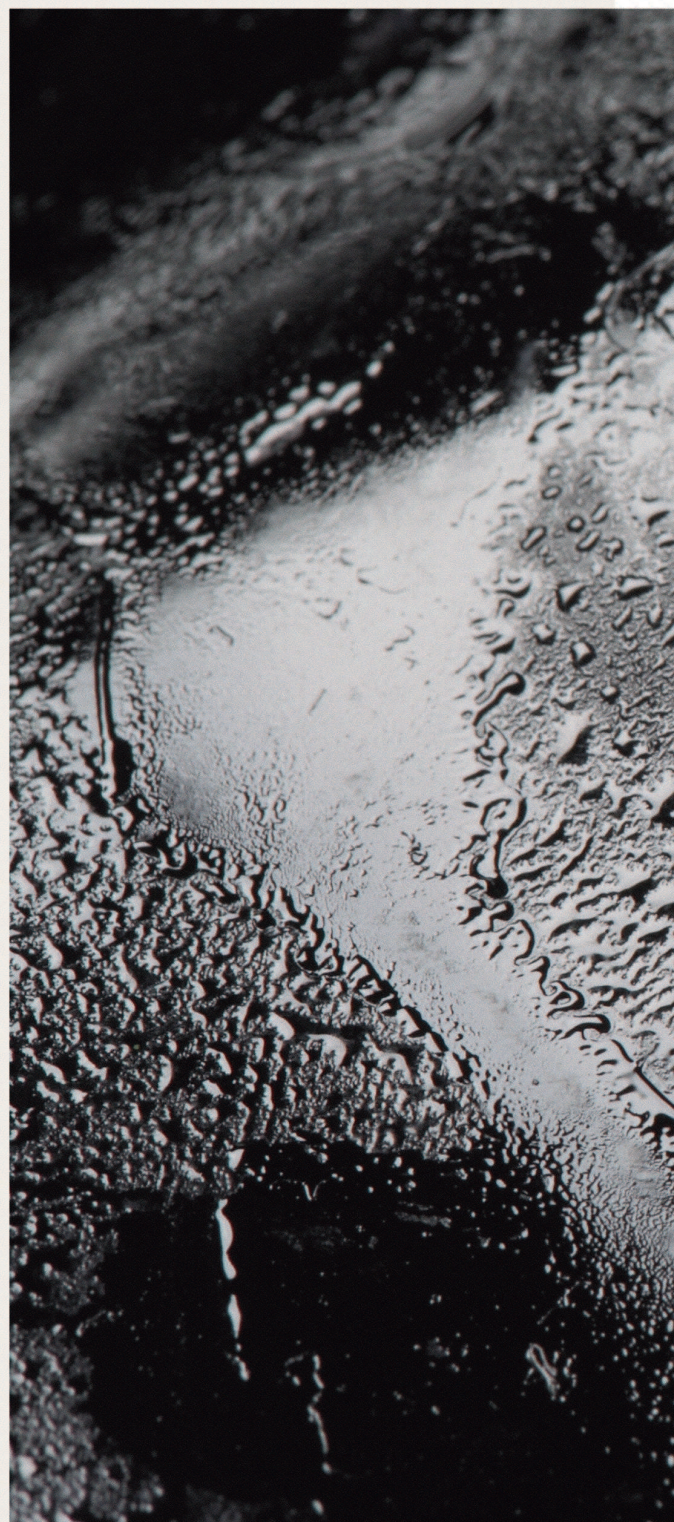


in a large package to protect it from dust, but the PVC stains and adheres to all the materials it contacts. PY-GCMS reveals that the drops are di-2-ethylhexyl phthalate (DEHP), a very common plasticiser for PVC. As another example of the raincoat kept by the musée du Peigne et de la plasturgie (Oyonnax, France) shows the same dramatic sweating, a larger amount of plasticiser in the formulation of material might be the probable cause of degradation. The last type of residues found on the objects surface is chemically unzipped polymer chain. Only one of the seventeen case studies has been unambiguously identified as such and was found on a suitcase textile coating: *La Valise des Nouveaux Réalistes* which contains several object made by Arman and other artists in 1973 (MAM, St-Etienne, museum number 90.11.1).

The outer polyester-based polyurethane coating (PUR ester) imitating a leather finish, is covered with spots of a thick layer of white particles that causes a whitish blooming on the surface (Figure 3). The pyrogram of the powder revealed the presence of two molecules: cyclopentanone and methylene-diphenyl diisocyanate. This data, combined with the findings from FTIR analysis allows concluding that the bloom is due to degraded and unzipped polyester-based polyurethane.

## b. Characterisation of VOCs

In order to assess volatiles emitted by artefacts, objects were selected at the musée d'Art moderne (St-Etienne) and the musée Galliera (Paris). The comb as well as the raincoat by P. Rabanne described previously were investigated because of the strong smell noticed in the vicinity of these objects. This study was carried out by using SPME-GCMS. It is a sensitive, reliable and non-invasive technique extensively used for collecting VOCs from a wide variety of matrices (Pawliszyn 1999), among which

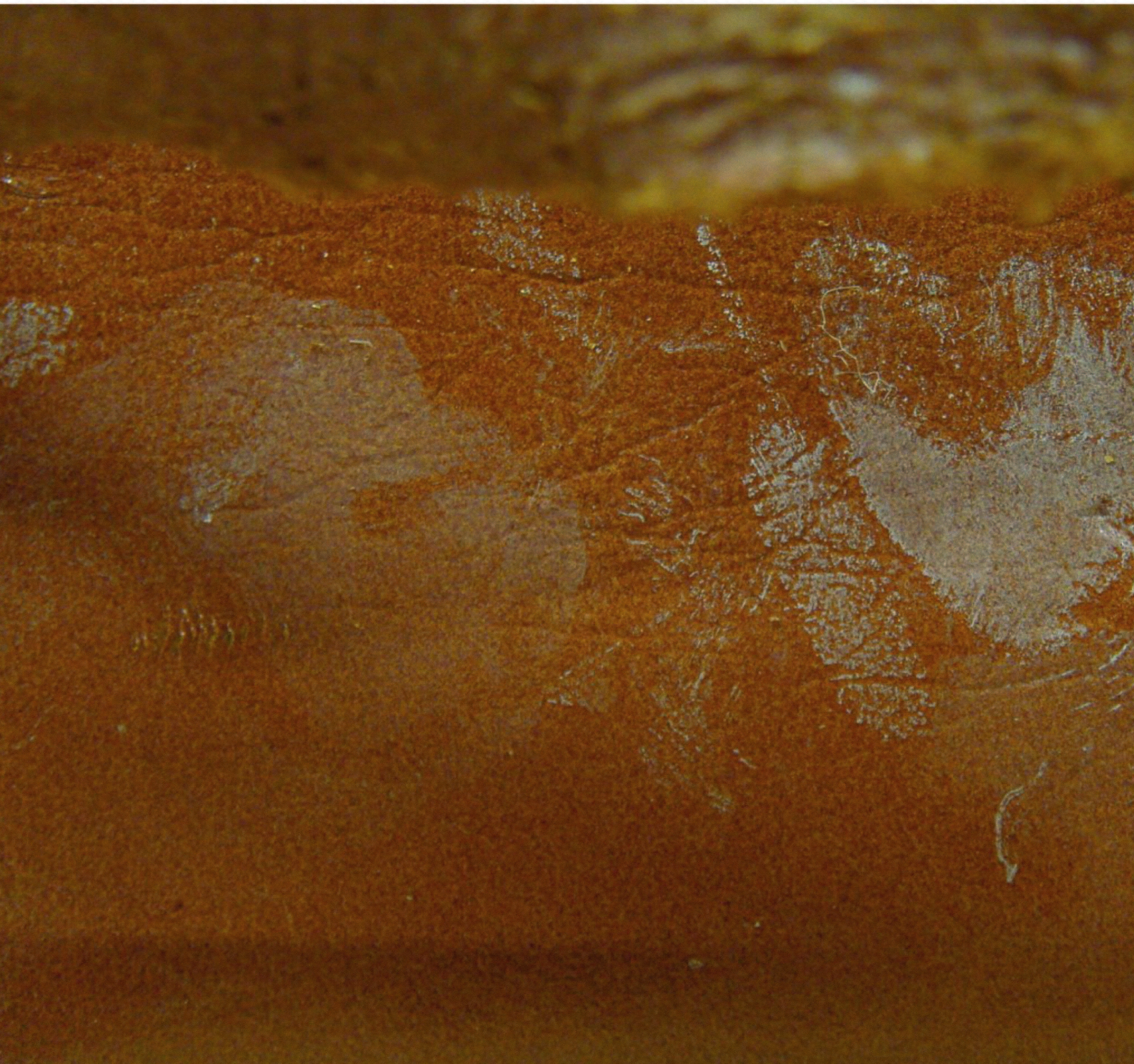






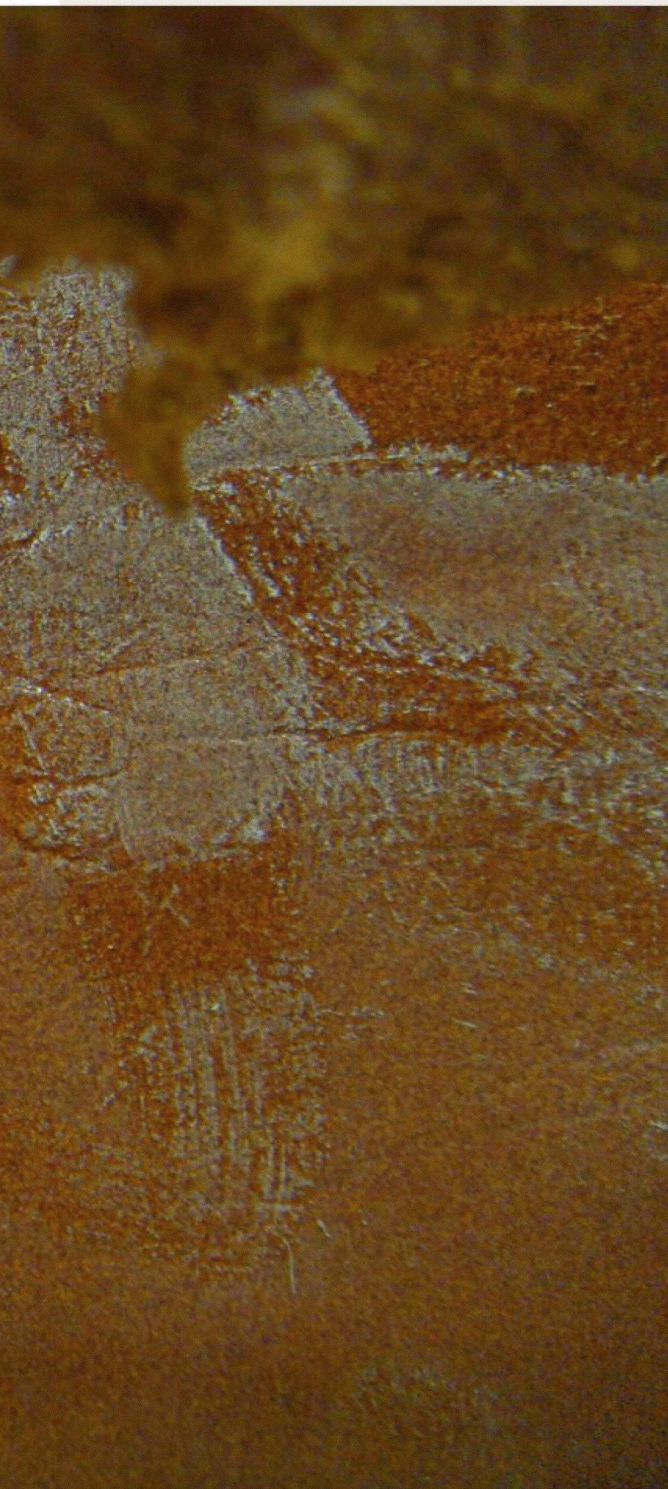
**Figure 2.** Paco Rabanne: Raincoat (detail). Drops of phthalate plasticisers on the surface of the PVC  
(© C2RMF, photo Thomas Clot)





**Figure 3.** Whitish blooming on a polyurethane ester imitation leather(© CRCC, photo Agnès Lattuati-Derieux)





are synthetic polymers (Albertsson *et al.*, 2006; Espert *et al.*, 2005; Gröning and Hakkarainen 2002; Hakkarainen 2008; Hakkarainen *et al.*, 2003; Thiébaud *et al.*, 2007). Analytical procedure used is described in the chapter 1. This research provided qualitative and semi-quantitative data and main results are briefly reported hereafter.

From the VOCs fingerprint of the comb, besides numerous other compounds, camphor was identified showing that it is still diffusing through the sample matrix. From the SPME extract of the coat, numerous phthalates, adipates and some other plasticisers such as 2,2,4-trimethyl-1,3-pentanediol diisobutyrate (TXIB) were detected in a relatively high amount. These VOCs can arise either from additives used for the manufacturing of the coat or from environmental pollutants. Most of these compounds are odoriferous which explain the strong smell. 2-ethylhexanol, which is generally considered to be a degradation product of di-2-ethylhexyl phthalate, was also detected, and its relative high amount might be related to the state of degradation of the plasticised poly(vinyl chloride).

One then applies this analytical methodology on two other museum artefacts stored at room temperature in uncontrolled environmental conditions, at the musée d'Art moderne (St-Etienne).

The first one is *Table et 6 chaises, module 400* made by Roger Tallon in 1965 (museum number 2008.6.1). The analysis was performed on polyether-based polyurethane flexible foam on the back of a chair (protected from direct light). This foam seemed to be in a good state of conservation upon visual examination. The chromatogram of the SPME extract showed the presence of compounds with glycol chemical structures mainly identified as ethylene glycol, propylene glycol, dipropylene glycol, tetrapropylene glycol and their monomethyl ether derivatives. These glycol derivatives are breakdown products produced by photo-oxidation of the polyol part of polyether-based polyurethanes, and can be considered as volatile markers of the state of degradation of the foam as the latter is sensitive mainly to light ageing. Their presence in relatively low amounts is well correlated with the good physical state of the foam of the chair.

The second artefact is the suitcase by Arman and other artists (museum number 90.11.1). The sample was polyester-based polyurethane flexible foam collected inside the suitcase. This foam was in a poor state of conservation. It had yellowed considerably





and showed a total loss of coherence resulting in powdering. The chromatogram of the SPME extract showed the presence of diethylene glycol. This compound is produced by the hydrolysis of the polyol part of polyester-based polyurethanes, which are sensitive mainly to hydrothermal ageing, and can be thus considered as a volatile marker of the state of degradation of the foam. Its presence in a relatively high amount is well correlated with the poor condition of the foam.

From these artefacts, the main degradation compounds that can be considered as volatile degradation markers of the natural deterioration of polyurethane flexible foams were trapped and identified.

As an achievement of the collection surveys led in three French museums, FTIR and Py-GCMS proved to be effective techniques for the characterisation of solid and liquid degradation products previously observed on the surface of objects. The analytical data obtained from samples also enabled identification of the substrate materials they come from in order to confirm assumptions made by naked eye observation. But they can only bring information on plastics already and obviously damaged, thus are not suitable to detect risk or prevent early damage. Early detection of VOCs emitted by the plastics being a prevention key issue for plastics conservation and for objects located in the vicinity, SPME-GCMS appeared as a sensitive and non-invasive method which is appropriate for *in situ* identification of volatile additives and other odoriferous compounds emitted by plastics from the first stages of their degradation process.

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