




# A preliminary approach for blooming removal in polyurethane-coated fabrics

## Uma abordagem preliminar para a remoção de eflorescências em tecidos revestidos com poliuretano

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### Abstract

Coated fabrics with thermoplastic polyurethane (TPU) are largely found in fashion and design collections in imitation leathers and glossy-look fabrics. Unfortunately, blooming is a common damage in aged TPU, appearing as white crystalline deposits at the surface. These deposits have been generally identified as adipic acid and mainly affect ester-based aromatic TPU. The white colour of adipic acid often leads to the complete unrecognition of the cultural item, highly decreasing its values. Strategies to remove blooming are still absent in the literature, resulting in a lack of action by conservators. The Glossy Surfaces project addressed this issue through preliminary research on cleaning strategies to remove adipic acid. Dry and wet methods were tested on two fabrics showing blooming and different surface cohesion. Non-confined and confined liquids in hydrogels were included and assessed by digital microscopy, colourimetry, and infrared spectroscopy. The best results were achieved with agar-agar, but limitations were also recognized.

### Resumo

Os tecidos revestidos com poliuretano termoplástico (TPU) são comumente encontrados em coleções de moda e design em capas e tecidos com brilho. Infelizmente, as eflorescências são um dano comum em TPU envelhecido, aparecendo como depósitos brancos cristalinos na superfície. Estes depósitos têm sido maioritariamente identificados como ácido adípico, afetando principalmente TPU de base aromática e éster. A cor branca do ácido adípico leva muitas vezes ao não reconhecimento do objeto cultural, diminuindo consideravelmente os seus valores. A literatura ainda não apresenta estratégias para remover eflorescências, o que resulta numa falta de ação dos conservadores. Este problema foi abordado preliminarmente pelo projeto Glossy Surfaces, através da avaliação de estratégias de remoção do ácido adípico. Foram testados métodos secos, húmidos e químicos, em tecidos com diferentes fragilidades. Incluíram-se líquidos não confinados e confinados em hidrogéis, avaliados por microscopia digital, colorimetria e espectroscopia de infravermelho. Os melhores resultados foram obtidos com agar-agar, tendo sido reconhecidas algumas limitações.

### KEYWORDS

White deposits  
 Cleaning  
 Adipic acid  
 Thermoplastic polyurethane  
 Coatings  
 Fashion and design

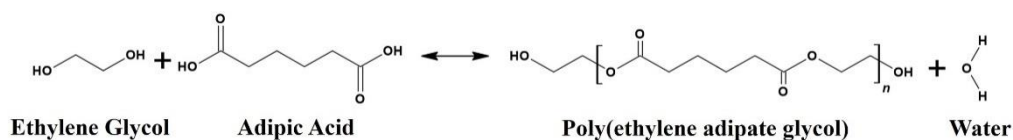
### PALAVRAS-CHAVE

Depósitos brancos  
 Limpeza  
 Ácido adípico  
 Poliuretano termoplástico  
 Revestimentos  
 Moda e design

## Introduction

Blooming is a damage frequently found in different substrates such as paintings, plastics, waxes, and rubbers [1-3]. It is defined as a white and crystalline deposit that appears at the surface of materials [4], caused by deterioration mechanisms such as the migration of additives or the formation of deterioration products through chemical reactions. In thermoplastic polyurethane (TPU) coated fabrics, blooming has been particularly found in coatings made of ester-based aromatic TPU [5-7]. A recent study on the application of infrared analysis [7] on TPU items with blooming confirmed this white product as adipic acid in 90 % of the analysed crystals, regardless of the substrate (genuine leather, cotton, polyamide, or polyester) or production date of the item (recent or older). The white colour of the salts of adipic acid leads to drastic visual changes of the coating's surface, severely affecting the aesthetic and exhibition value of the items featuring these materials, which is particularly problematic for museum collections [8]. Even though the whitening effect can be the first sign of alert of blooming in aged TPU-coated fabrics (impacting their aesthetic), their chemical and mechanical properties are also largely affected, possibly leading to material losses. In TPU coatings, adipic acid can be formed by the acid hydrolysis of the ester-rich segment in the TPU formulation, and its acidic nature (pH = 2.7) catalyses the ageing process of the coating material by feeding the chemical reaction [9-12].

TPU polymers are segmented structures comprising hard and soft segments chemically bonded along a linear macromolecular backbone [13-14]. The soft segment is rich in polyol, whereas the hard segment is rich in diisocyanate and chain extender. It is the reaction between the diisocyanate and the polyol that gives rise to the urethane bond and, therefore, to the name of this class of polymers. Depending on the chemical composition and mixing ratios of the initial raw materials, TPUs can exhibit a broad spectrum of hardness grades, allowing to produce soft, flexible, and elastomeric materials, as well as more brittle or high-modulus plastics [13]. In the TPU coatings chemistry, one of the most common polyol choices is the poly(ethylene adipate glycol), a hydroxyl-terminated polyester made from an esterification reaction between adipic acid (carboxylic acid) and the excess of ethylene glycol (alcohol), generically described in Figure 1 [13-15].



**Figure 1.** Examples of blooming visual appearance in TPU coated fabrics from fashion case studies produced: a) 1960s; b) 1970s; c) 1980s; d) 1990s; e) 2000s.

However, the esterification reaction is reversible, albeit slower [11-12], as the ester groups undergo hydrolytic attack. Previous studies on the hydrolytic ageing of ester-based polyurethanes have confirmed their susceptibility to humid conditions, leading to molecular weight loss (chain scission), formation of alcohol- and acid-based products, and viscosity changes [9-12, 16-17]. The formation of acidic products (such as adipic acid) makes the deterioration process autocatalytic [9-12].

As previously discussed, this deterioration results in the cultural item becoming unrecognizable to its creator, thereby reducing or even eliminating its potential for exhibition. The Glossy Surfaces project (2020-2023), composed of an international consortium of museums and research partners, focused on polyurethane-based materials in fashion and their conservation issues. TPU-coated fabrics were the most common and versatile material found in fashion collections, covering a wide spectrum of aesthetics, from imitation and patent leather textures to glossy, waterproof, sporty and metallic finishes [5-8]. The findings revealed a broader use of multi-layer TPU-coated fabrics in collections than anticipated and highlighted the challenges of preserving such materials. Careful assessments of numerous fashion items featuring TPU-coated fabrics revealed blooming in more than 60 % of the items, including

garments, shoes, and accessories [7]. Figure 2 shows examples of blooming in imitations of leather with glossy or suede-like textures assessed within the Glossy Surfaces Project.



**Figure 2.** Examples of blooming visual appearance in TPU coated fabrics from fashion case studies produced: a) 1960s; b) 1970s; c) 1980s; d) 1990s; e) 2000s.

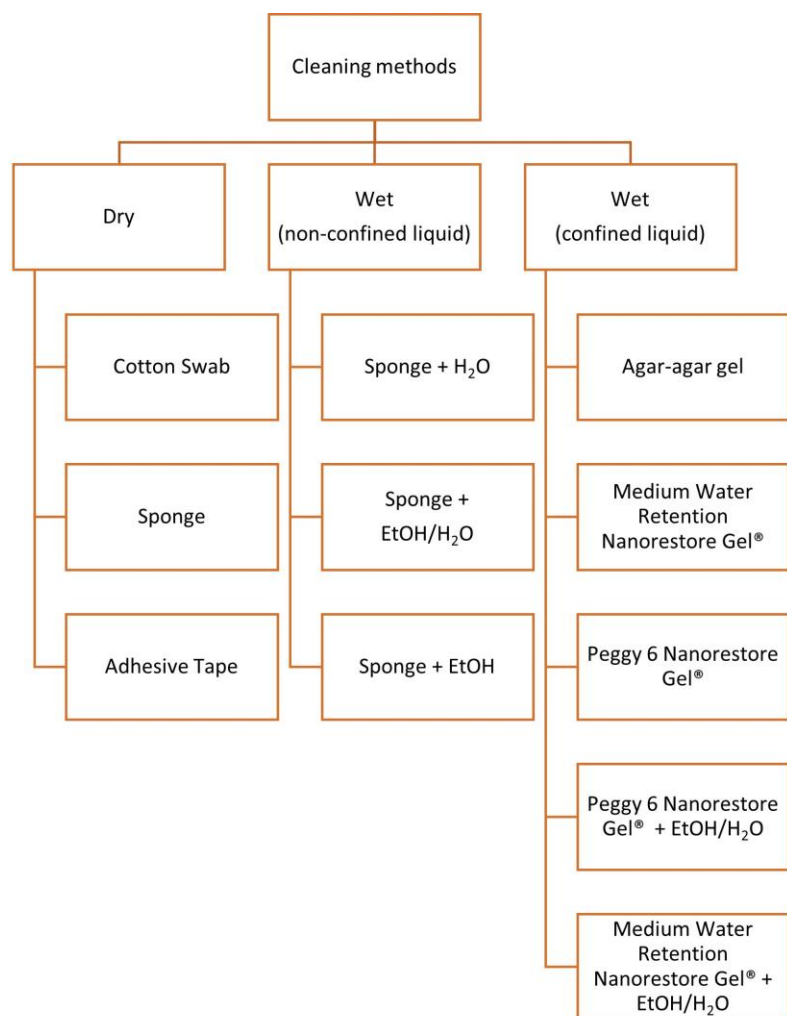
A pressing knowledge gap was also identified on the impact and removal of blooming from TPU, leading to an indefinite permanence of many deteriorated items in storage, without being displayed to the public. The few studies on the conservation-restoration of TPU-coated fabrics focus on consolidation treatments [18-19], and conservators still lack systematic knowledge on how to act on blooming in TPU-coated fabrics. Additionally, the few known attempts to remove blooming shared by some conservators during the collection of testimonies within Glossy Surfaces project indicated their short-term efficacy, as blooming tended to reappear after a relatively brief period.

For all these reasons, finding an efficient and safe solution for the removal of blooming was considered urgent, and was the focus of the present study. A preliminary approach to this goal started within the Glossy Surfaces project, with the assessment of both efficacy and safety criteria of a selected set of cleaning methods.

## Materials and methods

### Methodology

Dry and wet methods, the latter as confined (physical and chemical hydrogels) and non-confined liquids, were included in this study, as summarised in Figure 3. Two TPU-coated fabrics featuring blooming were selected, showing different levels of fragility on the top coating (see Materials section). Initially, all cleaning methods were tested on the less fragile TPU-coated fabric with blooming, with each method applied to separate areas. Methods deemed safe were then applied to the more deteriorated coated fabric using the same single-application approach per area. Only the two best methods were applied in triplicates, i.e. three times in three different areas on both TPU-coated fabrics (less and more fragile). The assessment was carried out before and after cleaning by digital microscopy, colourimetry, and infrared spectroscopy.



**Figure 3.** Scheme of the cleaning methods tested in the current study for the removal of blooming from ester-based aromatic TPU-coated fabrics.

## Materials and application methods

### *Solvents as cleaning agents*

Liquid cleaning agents were selected based on the solubility of adipic acid and the safety of the solvents for the ester-based aromatic TPU. According to [20-21], adipic acid is soluble in alcohols such as methanol and ethanol, although also being slightly soluble in water. Based on a study by BASF [22], ethanol is safer than methanol for ester-based TPUs, as it causes less swelling and less decrease of the polymer's tensile strength. This output resulted in the discard of methanol as a possible solvent. The same report [22] highlights water as the safest solvent for ester-based TPUs. Even though it has slight solubility power to adipic acid, water was also included in the current study in 100 % concentration and in combination with ethanol (50/50 %). For this study, distilled water and ethanol 96 % from Labchem were used.

### *Cleaning tools and gels*

As mechanical tools, custom-made cotton swabs on bamboo sticks, Kapton adhesive tape, and white high-density sponges (Deffner & Johann GmbH, (ca. 127 × 76 × 25 mm) were selected. According to infrared spectroscopy, the sponges were made of ether-based aromatic polyurethane foam with calcium carbonate; and the Kapton tape consisted of a polyimide carrier and a silicone-based adhesive. This yellowish tape was selected for its semi-transparency, leaving no residues at the surface and for having a medium adhesive power, being frequently used for collecting samples for analyses in conservation science. Soft sponges have been recommended as safe tools for the cleaning of sensitive surfaces [23]. The cotton swab was selected for comparison reasons with more traditional cleaning techniques.



To reduce the interaction of water with the TPU coating, three hydrogels (confined liquids) were included: agar-agar (Deffner & Johann GmbH), Peggy 6 and MWR (both from Nanorestore Gels). Agar-agar is a biopolymer and a physical rigid gel based on a polysaccharide extracted from red algae. It is slightly yellow, semi-transparent, completely non-toxic, easily available, and has already been tested in the cleaning of several substrates in cultural heritage [24-25] and according to [26], it does not leave residues at the surface. Agar-agar gel was prepared at 4 % in water, following the recipe described in [25]. Peggy 6 is an opalescent physical gel based on poly(vinyl alcohol) (PVAL). It is flexible and elastic, leaves no residues at the surface and is particularly suited for application on highly rough surfaces, having been recently tested in plastic substrates [27-28]. Medium Water Retention (MWR) gel is a dry and completely transparent chemical gel based on a poly(2-hydroxyethyl methacrylate)/poly(N-vinyl pyrrolidone) (pHEMA/PVP) semi-interpenetrated network, having very high retention of loaded liquid, and leaves no residues at the surface [29-30].

### **Cleaning application methods**

The cotton swabs were custom-made and prepared in the traditional way by rolling up an adequate amount of cotton fibres on the tips of bamboo sticks. They were applied dry on the coated fabric, and the surface was cleaned by slowly and carefully rolling the cotton swab without rubbing to minimise inducing additional damage to the coating.

The adhesive tape was applied to the surface of the coated fabric by gently pressing with the fingers to promote contact. It was then slowly and carefully removed by pulling one of the sides horizontally, as pulling vertically was concluded to be more damaging to the material as it promoted material loss.

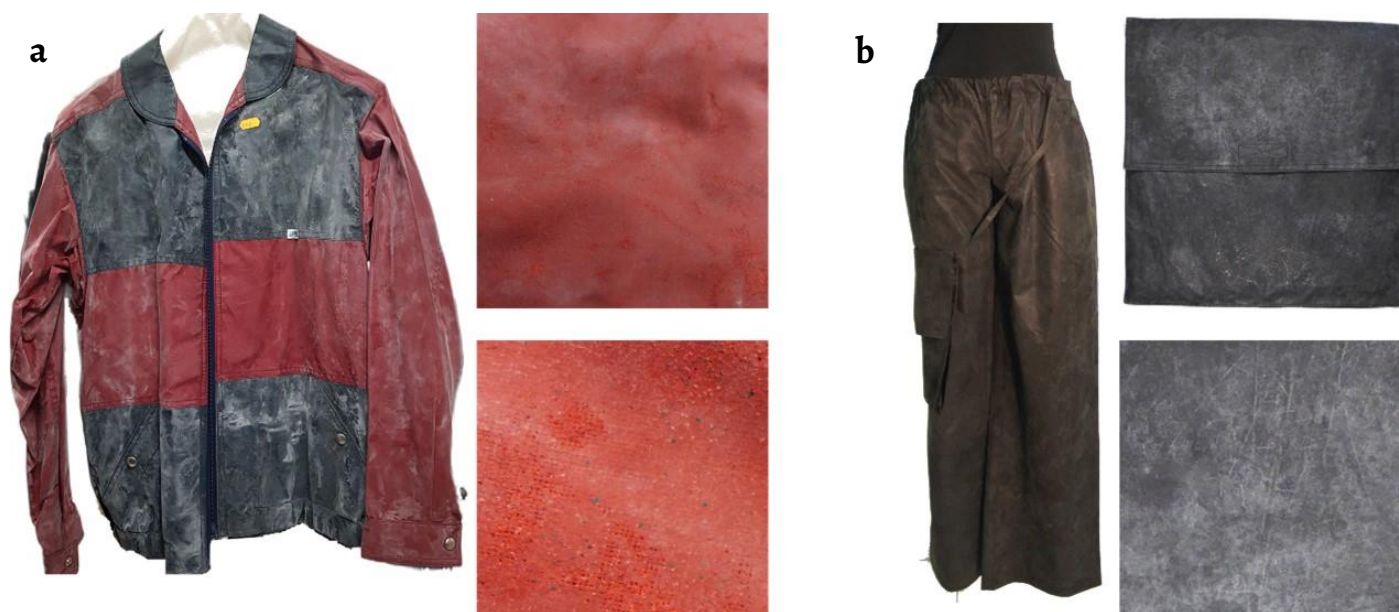
The high-density sponges were tested dry and wet, the latter with 100 % water, 96 % ethanol and a 50/50 % mixture of both solvents. Four drops of each solvent or solvent mixture were applied to the sponges and homogeneously spread by slightly pinching the sponge on its sides. The sponges were applied damp and not soaking wet to avoid excessively wetting the coating while still promoting the dissolution and removal of the adipic acid crystals. All sponges were tested similarly by repeatedly tapping the coating surface, applying gentle pressure to improve contact and lifting vertically without any rubbing.

Agar-agar gel was tested as prepared (see Cleaning tools and gels section). Peggy 6 and MWR were both tested as acquired and in a mixture of water and ethanol (50/50 %). All gels were similarly applied to the coating surface by gently pressing them for improved contact and left for 5 minutes without any additional weights or a polyester film on top. After the contact period, the gels were carefully lifted with the help of a spatula and easily removed. Each sample was only cleaned once with the respective gel.

Following the previously detailed procedure, the two best cleaning methods were also applied to the more degraded coated fabric.

### **TPU-coated fabric samples**

Two ester-based aromatic TPU-coatings in polyester substrates featuring blooming were selected (Figure 4). Although both exhibit blooming, one shows a more deteriorated condition with a fragile TPU coating that crumbles when handled, while the other is less deteriorated with a cohesive TPU coating. The latter is part of a fashion outfit designed by Portuguese designer Maria Gambina, consisting of a coated fabric pouch from an ensemble that also includes a pair of pants. This fashion outfit was considered a total loss by the designer due to the intensity of blooming and was donated to MUDE (The Design and Fashion Museum, Lisbon, Portugal) for research purposes. The item was left intact and 4 cm windows at the back were cleaned following the selected methods. The highly fragile TPU coating case study was purchased and consisted of a red and black jacket, of which red squares of 4 cm were cut to be cleaned following the different methods.



**Figure 4.** Selected TPU-coated fabric case studies featuring blooming for the cleaning study, with different TPU cohesion: *a*) a fragile TPU coating that crumbles when handled; *b*) a still cohesive TPU coating (pouch belonging to Maria Gambina's ensemble). Detailed images of the condition of the TPU-coated fabrics are shown close to the piece (top ones: naked eye, bottom ones with magnification  $\sim 10\times$ ).

### Instrumentation

Colour measurements were performed using a Konica Minolta CR-410 Colourimeter. The optical system of the measuring head uses diffuse illumination from a pulsed Xenon lamp over a 50mm diameter measuring area,  $10^\circ$  viewing angle geometry and D65 illuminant. Calibration was performed with bright white and black standard plates, and all values were collected with the specular component excluded (SCE). To follow the cleaning efficacy, the  $L^*$  value (ranging from 0 (black) to 100 (white)) [31] was specifically selected and followed due to the white colour of adipic acid. From  $L^*$  values, Delta  $L^*$  was calculated ( $\Delta L^* = L_{\text{after cleaning}} - L_{\text{before cleaning}}$ ). Each sample's colour was measured three times at the centre, before and after cleaning.

Digital imaging before and after cleaning was carried out with the portable digital optical microscope Dino-Lite AM73115MTF. The cleaning tools/vehicles (cotton swab, adhesive tape, sponges, and gels) were also photographed after cleaning to assess their safety in the cleaning procedure. Each sample was photographed using a custom-made cardboard frame/mask with an area of  $2 \text{ cm}^2$ . The images presented are representative of the main results per cleaning method.

Infrared spectroscopy in attenuated total reflection mode (ATR-FTIR) was carried out with the handheld Agilent 4300 spectrophotometer (Agilent, Santa Clara, US), equipped with a ZnSe beam splitter, a Michelson interferometer, and a thermoelectrically cooled DTGS detector. Spectra between  $4000$  and  $650 \text{ cm}^{-1}$  were acquired with a diamond ATR module, 128 scans and  $4 \text{ cm}^{-1}$  resolution. Background spectra (air) were collected between every acquisition.

As adipic acid is formed through hydrolytic attack, it was important to assess if aqueous cleaning would imply an increase in the water content of the fabrics, possibly promoting blooming in the future. Since no equipment capable of directly measuring the water content of synthetic-coated fabrics was available, an approximation to this goal was achieved through gravimetric measurements taken before and after cleaning. For that, two additional coated fabrics composed of ester-based aromatic TPU-coatings and polyester substrates were included. It is important to highlight that although these fabrics showed a similar chemical composition to the ones used for the cleaning trials, they did not show blooming or other types of deposits because the goal was to only assess changes in water content and not cleaning efficacy, since the removal of adipic acid would lead to misinterpretation of the results. The two TPU-coated fabrics differed in their condition: one did not show visual signs of deterioration, and the other was severely deteriorated by flaking (delamination of the coating in small


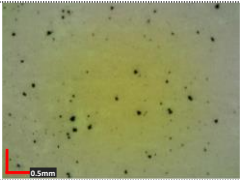
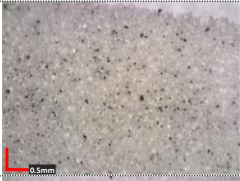


fragments). This was considered relevant because many fashion items with blooming also show flaking or cracking areas, which can increase water penetration and consequent increase in evaporation time. The mass (mg, resolution of 0.01 mg) of the samples was measured before and after cleaning with a sponge slightly dampened with water. The amount of water per sponge (1 ml) and the number of passages (10 for each sample) was kept constant between cleaning trials. Non-cleaned samples were included as controls and all samples were kept in open air in the lab during the entire process. Sample weight determinations (mg, 0.01) were obtained with a Sartorius CP225 D micro analytical scale. Three independent measurements were performed per coated fabric.

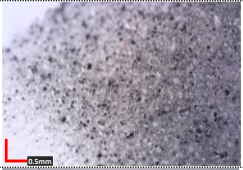

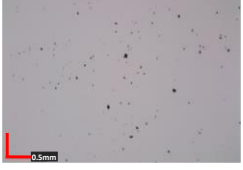
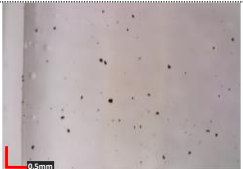



## Results and discussion

### Assessing cleaning strategies

Delta L\* ( $\Delta L^*$ ) values for all cleaning methods are summarised in Table 1, as well as the acquired image of the tool/vehicle after cleaning, which allows the comparison between efficacy ( $\Delta L^*$ ) and safety (TPU black or red particles collected by the cleaning tool/vehicle) in the short-term for all cleaning procedures. It is important to emphasise that a higher  $\Delta L^*$  value (most negative value) corresponds to a better efficacy of the cleaning strategy, as more adipic acid would have been removed, turning the sample less white in colour. A less safe cleaning method will correspond to a higher number of black or red particles in the tool/vehicle image after cleaning, as more TPU would have been removed.

**Table 1.** Variation of L\* ( $\Delta L^*$ ) coordinate values and image of the cleaning tool/vehicle after blooming removal.

Sample	Cleaning method	$\Delta L^*$	Tool/Vehicle after cleaning
Less deteriorated TPU-coated fabric (black pouch)	Dry Cotton swab	-0.90	
	Adhesive tape	-2.12	
	Sponge	-2.11	
	Wet   Non-confined liquid Sponge + H <sub>2</sub> O	-5.89	
	Sponge + H <sub>2</sub> O/EtOH (50/50 %)	-4.00	

		Sponge + EtOH (96 %)	-3.50	
	Wet   Confined liquid	Agar-agar	-6.27	
		Peggy 6	-2.97	
		MWR	-3.47	
		Peggy 6 + H <sub>2</sub> O/EtOH (50/50 %)	-3.17	
		MWR + H <sub>2</sub> O/EtOH (50/50 %)	-3.03	
				Sponge + H <sub>2</sub> O
More deteriorated TPU-coated fabric (black and red jacket)	Wet   Confined liquid	Agar-agar	-5.11	

As presented in Table 1, the three dry-cleaning methods tested (cotton swab, sponge, and adhesive tape) demonstrated reduced safety as a large amount of TPU particles was removed upon cleaning. In general, the dry-cleaning methods also showed a reduced efficacy ( $\Delta L^* \leq -2.12$ ) when compared to the wet ones, both non-confined and confined. A small amount of adipic acid was removed, and all tools showed TPU particles after cleaning. The cotton swab was even confirmed as the worst method as a large number of fibres were detected on the TPU coating after cleaning (Figure 5), being immediately discarded for further tests. The soft sponge was selected for further testing as its reduced safety could be improved with the addition of a liquid cleaning agent.

The soft sponge was then tested as a wet cleaning tool by its humidification in water, ethanol and a mixture of both solvents (50/50 %). In general, and in agreement with the literature [22], water proved to be safer than ethanol: water alone resulted only in a small amount of TPU removal during cleaning, whereas the use of 96 % of ethanol was catastrophic for the safety of the TPU coating, removing a great number of particles (Table 1), even when applied on the less



deteriorated TPU coating. The best method within this class of non-confined liquids was the sponge with water because it was able to remove a significant amount of adipic acid ( $\Delta L^* = -5.89$ ) without causing a large loss of TPU coating (Table 1 and Figure 6).

This was also observed with the use of ethanol; contrary to expectations, loading ethanol into the Nanorestore Gels did not significantly enhance their cleaning efficacy. Once more, this was probably related to the high retentive power of these gels, especially during a short time of interaction with the substrate (5 min).

Considering the collected data, the two best methods, the sponge with water and the agar-agar gel, were applied on the more fragile TPU-coated fabric (Table 1 and Figure 7). The tool image after cleaning observed in Table 1 shows that the sponge/water cleaning system resulted in a reduced safety when compared to agar-agar gel, since the mechanical action of the sponge promoted material loss of the highly fragile TPU coating. On the other hand, agar-agar provided good efficacy and safety (Table 1 and Figure 7), as almost no TPU particles were removed during cleaning and a significant reduction of the  $\Delta L^*$  was verified.

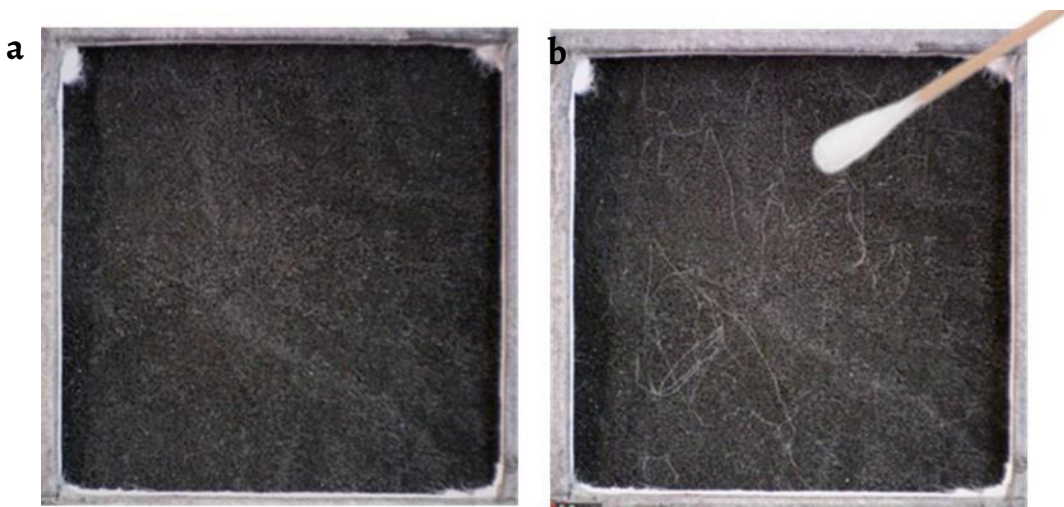


Figure 5. Less deteriorated TPU-coated fabric with blooming: a) before and b) after dry-cleaning with a cotton swab.

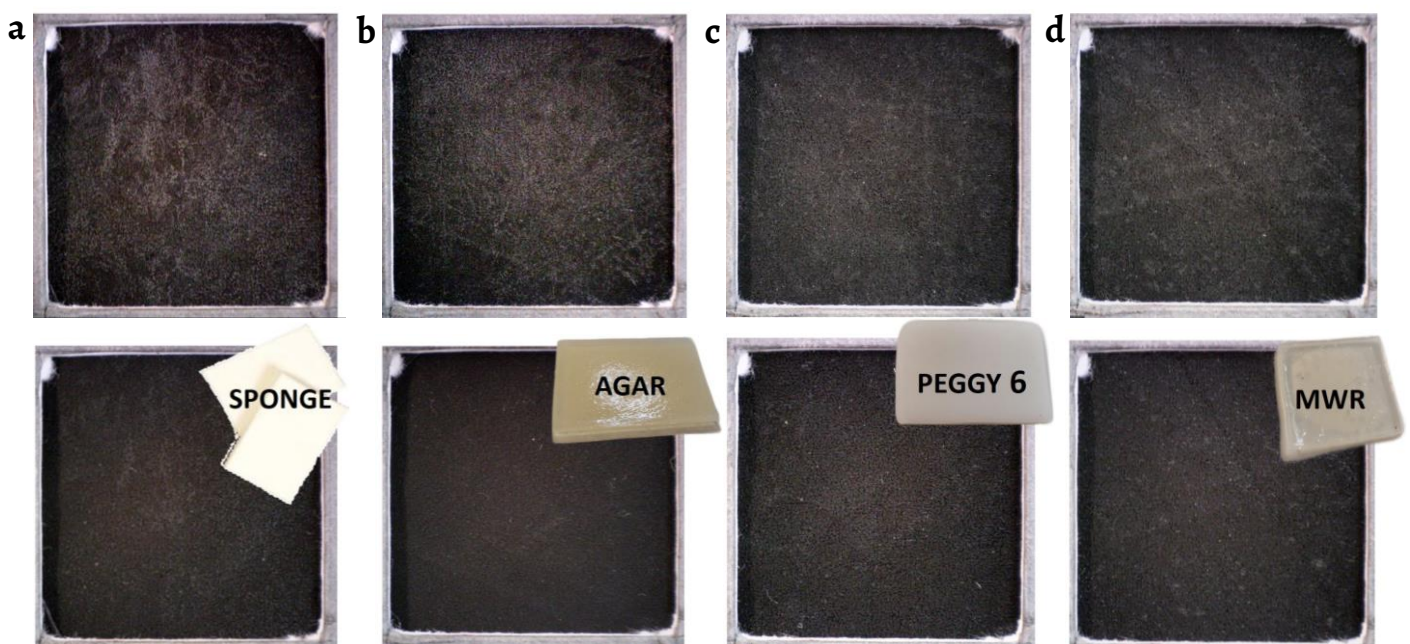
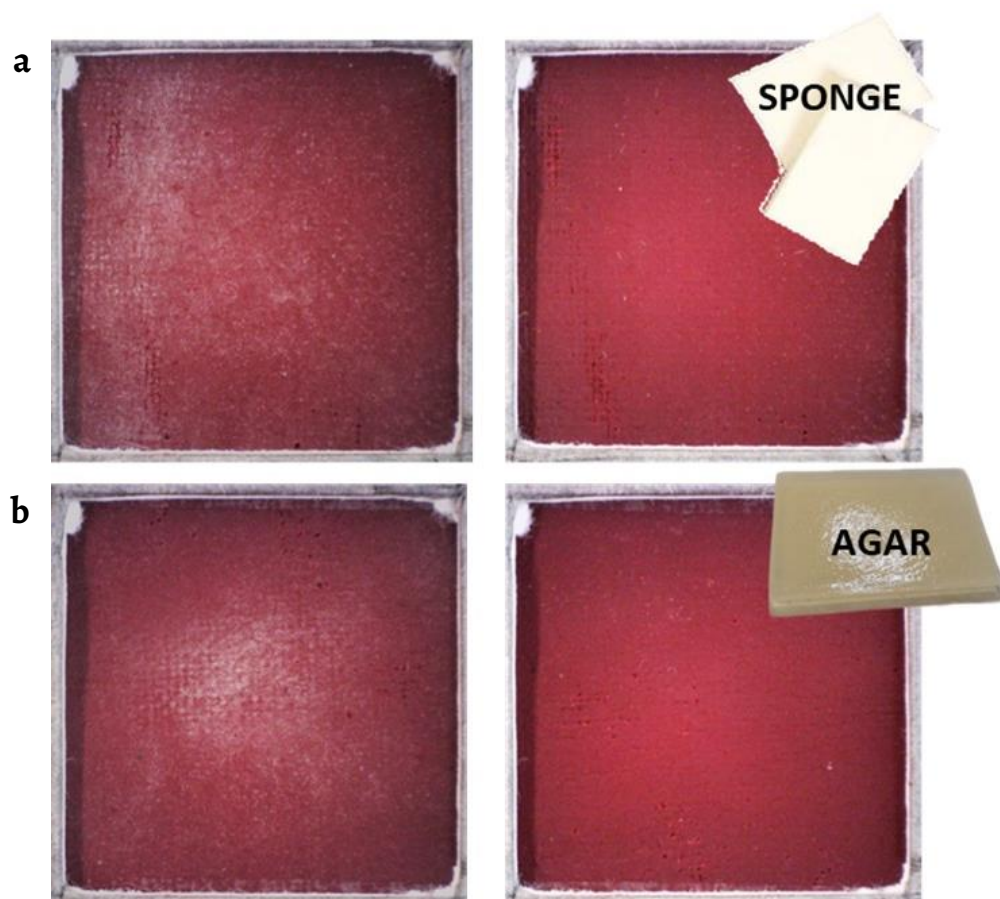


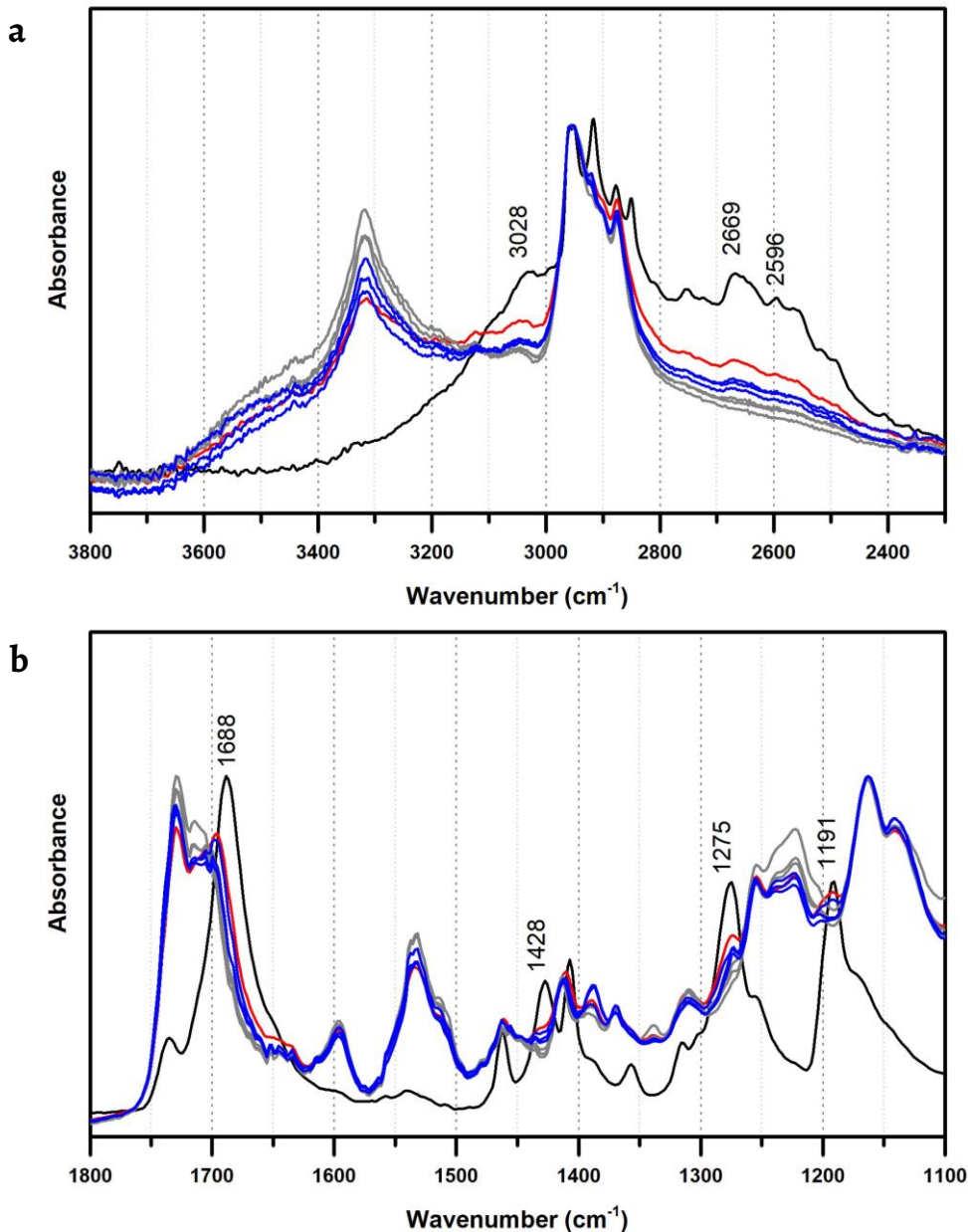
Figure 6. Less deteriorated TPU-coated fabric with blooming, before (top) and after (bottom) wet cleaning methods: a) sponge with water; b) agar-agar; c) Peggy 6; d) MWR.



**Figure 7.** More deteriorated TPU-coated fabric with blooming, before (left) and after (right) cleaning with the best identified wet cleaning methods: *a*) sponge/water and *b*) agar-agar gel.

The two best procedures were also assessed by infrared spectroscopy. As this study launched a new possibility of recovering the exhibition potential of the black ensemble by Maria Gambina, previously considered a total loss, ATR-FTIR analysis were only conducted on the more fragile item. As known, the intimate contact of the ATR crystal with the cleaned windows of Maria Gambina's item would cause indentations and damages, thus this procedure was discarded.

Based on infrared spectroscopy (Figure 8), it was possible to assess the homogeneity and in-depth efficacy of the two best methods, the sponge/water system and the agar-agar gel. Curiously, even though colorimetry suggested the sponge/water system as a high efficacy method in the removal of blooming, ATR-FTIR allowed the detection of spectral lines still assigned to adipic acid in the TPU-coated samples cleaned with this method: composite-profile at circa  $3000\text{ cm}^{-1}$  and bands at c.  $1689$ ,  $1276$  and  $1192\text{ cm}^{-1}$  (assigned to O-H, C=O, -C-O and stretching of adipic acid, respectively [32-35]) (Figure 8). On the other hand, the three spectra of the TPU-coated samples cleaned with agar-agar showed none or only small traces of these bands (Figure 8), possibly indicating a higher efficacy and homogeneity of the cleaning procedure.

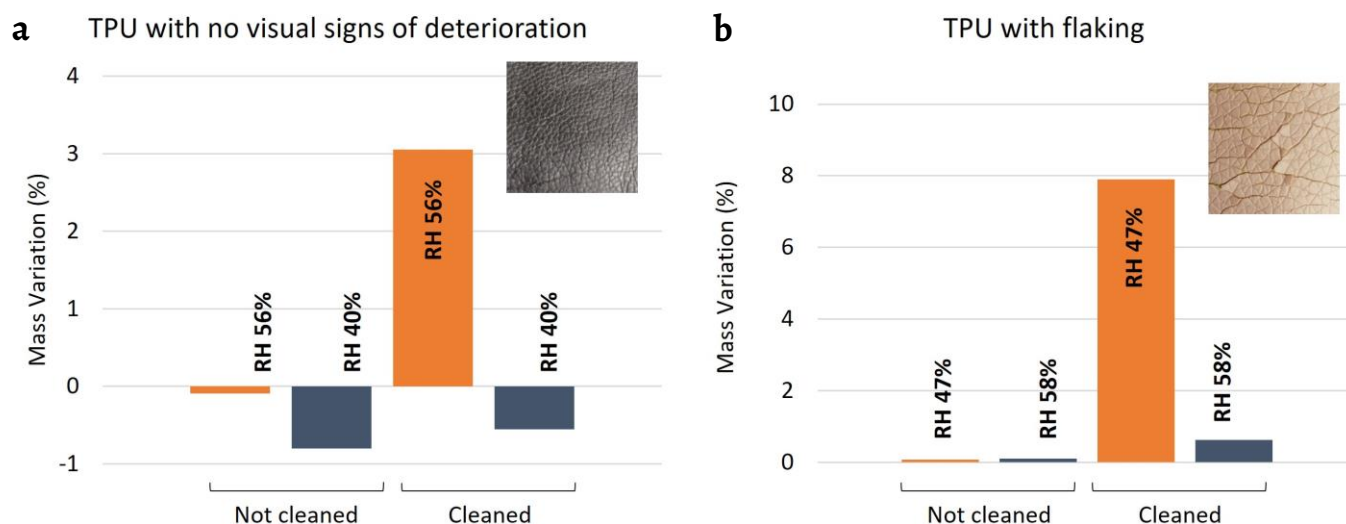


**Figure 8.** Infrared spectra (ATR-FTIR) of the highly fragile TPU-coated fabric featuring blooming after cleaning with sponge/water (blue) and agar-agar gel (grey): *a*) between 3800 and 2300 $\text{cm}^{-1}$ ; *b*) 1800 and 1100  $\text{cm}^{-1}$ . Black line corresponds to adipic acid spectrum and red line to a representative spectrum of a non-cleaned sample.

### Assessing water safety as cleaning agent

As the formation of adipic acid in ester-based TPUs is addressed in the literature as a result of the hydrolytic attack to the ester-rich segment, as previously mentioned, determining the water content in samples before and after aqueous cleaning was considered significant. The chosen strategy to follow these values was through mass measurement to assess whether water was retained in the sample after cleaning. **Figure 9** shows the mass variation (%) of the two tested TPU-coated fabrics (one with no visual signs of deterioration, and another with flaking) after 1 hour and 1 day of cleaning. The relative humidity (RH) of the room was registered before all mass measurements. From the control non-cleaned samples, it was possible to observe that RH fluctuations of 15 % (between first and final measurement) were enough to cause mass variations of 1 % in the samples, which can be related to the hydrophilic nature of these TPU-coated fabrics. Also, as expected, the most deteriorated samples showed a higher mass variation right after cleaning, as surface contact with more layers of the coated fabric increases drastically, but after 1 day the original weight was almost totally recovered.





**Figure 9.** Mass variation (%) measurements of TPU-coated samples (cleaned and not cleaned) after 1 h (orange bars) and 1 day (grey bars): a) TPU with no signs of deterioration; b) TPU with flaking Inset: images of the TPU-coated samples submitted to this assessment.

### Limitations of the study and future work

Even though water proved to be the safest cleaning solvent, it is important to consider that the use of water may also lead to an increase in surface acidity, with medium- or long-term implications, which were not the focus of the current study. Also, even though pH measurements before and after cleaning were carried out at the beginning of the study, the requirement of a water drop, and consequent adipic acid dissolution led to inconclusive results and to the discarding of the technique.

Although agar-agar gel showed promising results, it is important to highlight that all TPU-coated fabrics tested had a smooth, flat texture. The efficacy of this cleaning procedure should also be confirmed in different coating textures, as well as in TPU-coated fabrics with more intense levels of blooming. Also, the transition of a lab-scale study to the cleaning of real and/or complex-shaped objects should also be addressed in future research, starting from this promising study.

Research is being carried out to assess the impact of storage conditions in the reappearance of blooming after its removal. After circa 6 months, no clear reappearance has been noticed, independently on the storage condition (open-air, enclosed in anoxic, wrapped in cotton, and wrapped in silicone-coated polyester film) [36]. Results regarding the passage of 12 months will be collected and disseminated soon.

### Conclusion

This is the first study addressing the removal of blooming as adipic acid from TPU-coated fabrics, representing a preliminary approach to a damage largely found in fashion and design collections. Several cleaning methods were tested: dry cleaning with adhesive tape, sponge and cotton swab, and wet cleaning with water and ethanol in confined (hydrogels) and non-confined (sponges) systems. To increase the representativeness of the results, two TPU-coated fabrics featuring blooming were included: one in a more advanced deterioration condition, showing a highly fragile TPU coating; the other in a less deteriorated state with a still cohesive TPU coating. In agreement with the literature, water proved to be the safest solvent in the short-term, while ethanol resulted in a high removal of TPU particles. Within the selected methods, agar-agar gel was, so far, the best cleaning procedure in terms of safety and efficacy, as pointed out by visual, colour and molecular assessment, as it did not promote material loss of the TPU coatings while efficiently removing the deposited adipic acid crystals. However, the



rigidity of agar-agar gel might pose a disadvantage in cleaning rougher textures when compared to the soft sponge, as the gel might not conform to the irregular surface of these materials, compromising the efficacy of the procedure. This launches further research lines, which should be focused on the assessment of novel methods for the application of the agar-agar, such as in spray, as recently published in literature for other substrates [26]. Additionally, and of high importance, the long-term safety and efficacy of the most successful cleaning methods should be investigated, specifically focusing on the potential impact of water on promoting acidity in TPU.

Other chemical natures of blooming (lubricants such as adipates) also identified in previous research [7] on TPU-coated fabrics were not included in this study, so prior identification is mandatory before testing the efficiency of these methods.

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#### REFERENCES

- Puglieri, T. S.; Lavezzo, A. S.; dos Santos, I. F.; de Faria, D. L. 'Investigation on the hazing of a Brazilian contemporary painting', *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **159** (2016) 117-122, <https://doi.org/10.1016/j.saa.2016.01.035>.
- Bartl, B.; Kobera, L.; Drábková, K.; Ďurovič, M.; Brus, J., 'Wax bloom' on beeswax cultural heritage objects: Exploring the causes of the phenomenon', *Magnetic Resonance in Chemistry* **53**(7) (2015) 509-513, <https://doi.org/10.1002/mrc.4244>.
- Krieg, T.; Mazzon, C.; Gómez-Sánchez, E., 'Material analysis and a visual guide of degradation phenomena in historical synthetic polymers as tools to follow ageing processes in industrial heritage collections', *Polymers* **14**(1) (2021) 121, <https://doi.org/10.3390/polym14010121>.
- Lavédrine, B.; Fournier, A.; Martin, G. (eds.), POPART: Preservation of plastic artefacts in museum collections, Comité Des Travaux Historiques Et Scientifiques (CTHS), Paris (2012).
- França de Sá, S.; Verkens, K.; Rizzo, A.; Petersen, G.; Scaturro, S.; Correia, I.; Carita, M., 'Synthetic coatings in fashion collections: identification and preservation issues', in *Handbook of museum textiles*, eds. S. Jose, S. Thomas, P. Pandit & R. Pandey, vol 2, Scrivener Publishing LLC, Hoboken (2023) 319-344, <https://doi.org/10.1002/9781119983903>.
- Rizzo, A.; Scaturro, S., 'Already out of fashion: The fashionable rise and chemical fall of thermoplastic polyurethane', in *Transcending boundaries: integrated approaches to conservation. ICOM-CC 19th Triennial Conference Preprints*, ed. J. Bridgland, ICOM-CC, Beijing (2021), [ICOM-CC Publications Online \(icom-cc-publications-online.org\)](https://icom-cc-publications-online.org) (accessed 25-07-2024).
- França de Sá, S.; Ferreira, J. T.; van der Velde, E.; Correia, I.; Rizzo, A.; Verkens, K., 'Mapping polyurethane coated fabrics and damages in fashion collections worldwide by optical microscopy and infrared spectroscopy', in *Semi-synthetic and synthetic textile materials in fashion, design and art*, ICOM-CC Modern Materials & Contemporary Art and Textiles Working Groups Joint Interim Meeting 21-23 Feb 2023, submitted (n.d.).
- França de Sá, S.; Ramos, A. M.; Macedo, R.; Ferreira, J. L.; Coutinho, B., 'How to keep what was intended to be temporarily functional? Reflections on decision-making for the conservation of polyurethane ready-to-wear fashion', in *Authenticity and Replication the 'real thing' in art and art conservation*, eds. R. Gordon, E. Hermens & F. Lennard, Archetype Publications, London (2014) 193-203.
- Rychlý, J.; Lattuati-Derieux, A.; Lavédrine, B.; Matisová-Rychlá, L.; Malíková, M.; Csomorová, K.; Janigová I., 'Assessing the progress of degradation in polyurethanes by chemiluminescence and thermal analysis. II. Flexible polyether- and polyester-type polyurethane foams', *Polymer Degradation and Stability* **96** (2011) 462-469, <https://doi.org/10.1016/j.polyimdegradstab.2011.01.012>.
- Lattuati-Derieux, A.; Thao-Heu, S.; Lavédrine, B., 'Assessment of the degradation of polyurethane foams after artificial and natural ageing by using pyrolysis-gas chromatography/mass spectrometry and headspace-solid phase microextraction-gas chromatography/mass spectrometry', *Journal of Chromatography A* **1218**(28) (2011) 4498-4508, <https://doi.org/10.1016/j.chroma.2011.05.013>.
- Schollenberger, C. S.; Stewart, F. D., 'Thermoplastic polyurethane hydrolysis stability', *Journal of Elastoplastics* **3**(1) (1971) 28-56, <https://doi.org/10.1177/009524437100300103>.
- Mondal, S.; Martin, D., 'Hydrolytic degradation of segmented polyurethane copolymers for biomedical applications', *Polymer degradation and stability* **97**(8) (2012) 1553-1561, <https://doi.org/10.1016/j.polyimdegradstab.2012.04.008>.
- Meckel, W.; Goyert, W.; Wieder, W., 'Thermoplastic Polyurethane Elastomers', in *Thermoplastic Elastomers*, eds. G. Holden, N.R. Legge, R. Quirk & H.E. Schroeder, 2nd ed, Carl Hanser Verlag, Munich (1996) 16-17.
- Yilgör, I.; Yilgör, E.; Wilkes, G. L., 'Critical parameters in designing segmented polyurethanes and their effect on morphology and properties: a comprehensive review', *Polymer* **58** (2015) A1-A36, <https://doi.org/10.1016/j.polymer.2014.12.014>.

15. BASF SE, *Soft thermoplastic polyurethane elastomers and process for their preparation*, European Patent Office, patent number EP3004198A1, Germany, BASF SE (2016).
16. Pellizzi, E.; Lattuati-Derieux, A.; Lavédrine, B.; Cheradame C., 'Degradation of polyurethane ester foam artifacts: Chemical properties, mechanical properties and comparison between accelerated and natural degradation', *Polymer Degradation and Stability* **107** (2014) 255-261, <https://doi.org/10.1016/j.polymdegradstab.2013.12.018>.
17. Pellizzi, E.; Lattuati-Derieux, A.; d'Espinose de Lacaillerie, J-B.; Lavédrine, B.; Cheradame, H., 'Consolidation of artificially degraded polyurethane ester foam with aminoalkylalkoxysilanes', *Polymer Degradation and Stability* **129** (2016) 106-113, <https://doi.org/10.1016/j.polymdegradstab.2016.04.007>.
18. Bechthold, T.; Rogerson, C.; Garside, P., 'Wet look in 1960s furniture design: degradation of polyurethane-coated textile carrier substrates', in *The future of the 20th century, collecting, interpreting and conserving modern materials. Postprints of AHRC Research Centre for Textile Conservation and Textile Studies*, ed. C. Rogerson & P. Garside, Archetype Publications, London (2006) 128-133.
19. Schertel, B., *Polyurethane-coated textiles found on furniture from the 1960s and 1970s: their manufacture, deterioration and consolidation*; Master dissertation, Furniture Conservation, Victoria & Albert Museum / Royal College of Art, London (2006).
20. Gaivoronskii, A. N.; Granzhan, V. A., 'Solubility of adipic acid in organic solvents and water', *Russian journal of applied chemistry* **78**(3) (2005) 404-408, <https://doi.org/10.1007/s11167-005-0305-0>.
21. Zhibo, M.; Xiaobo, S.; Xianghai, L.; Yu, W.; Guoji, L., 'Measurement and correlation of solubilities of adipic acid in different solvents', *Chinese Journal of Chemical Engineering* **17**(3) (2009) 473-477, [https://doi.org/10.1016/S1004-9541\(08\)60233-5](https://doi.org/10.1016/S1004-9541(08)60233-5).
22. BASF Polyurethanes GmbH, 'Thermoplastic Polyurethane Elastomers (TPU) Elastollan® – Chemical Resistance', in *Technical Information* (2011), [https://www.campusplastics.com/file/show/59/0/5e\\_TPU\\_ChemRes.pdf](https://www.campusplastics.com/file/show/59/0/5e_TPU_ChemRes.pdf) (accessed 2024-02-20).
23. Daudin-Schotte, M.; van Keulen, H., 'Dry cleaning: research and practice', in *Issues in contemporary oil paint*, eds. K. van den Berg, A. Burnstock, M. de Keijzer, T. Learner, A. Tagle & G. Heydenreich, Springer International Publishing Switzerland, Switzerland (2014) 363-372, [https://doi.org/10.1007/978-3-319-10100-2\\_24](https://doi.org/10.1007/978-3-319-10100-2_24).
24. Sansonetti, A.; Bertasa, M.; Canevali, C.; Rabbolini, A.; Anzani, M.; Scalarone, D., 'A review in using agar gels for cleaning art surfaces', *Journal of Cultural Heritage* **44** (2020) 285-296, <https://doi.org/10.1016/j.culher.2020.01.008>.
25. Casoli, A.; Cremonesi, P.; Isca, C.; Groppetti, R.; Pini, S.; Senin, N., 'Evaluation of the effect of cleaning on the morphological properties of ancient paper surface', *Cellulose* **20** (2013) 2027-2043, <https://doi.org/10.1007/s10570-013-9975-6>.
26. Giordano, A.; Caruso, M. R.; Lazzara, G., 'New tool for sustainable treatments: agar spray—research and practice', *Heritage Science* **10**(1) (2022) 123, <https://doi.org/10.1186/s40494-022-00756-9>.
27. Shashoua, Y.; Alterini, M.; Pastorelli, G.; Cone, L., 'From microfibre cloths to poly (vinyl alcohol) hydrogels—conservation cleaning of plastics heritage', *Journal of Cultural Heritage* **52** (2021) 38-43, <https://doi.org/10.1016/j.culher.2021.08.009>.
28. Angelova, L. V.; Sofer, G.; Bartoletti, A.; Ormsby, B., 'A comparative surface cleaning study of op structure, an op art PMMA sculpture by Michael Dillon', *Journal of the American Institute for Conservation* **62**(1) (2023) 58-77, <https://doi.org/10.1080/01971360.2022.2031459>.
29. Domingues, J.; Bonelli, N.; Giorgi, R.; Fratini, E.; Gorel, F.; Baglioni, P., 'Innovative hydrogels based on semi-interpenetrating p(HEMA)/PVP networks for the cleaning of water-sensitive cultural heritage artefacts', *Langmuir* **29**(8) (2013) 2746-2755, <https://doi.org/10.1021/la3048664>.
30. Domingues, J.; Bonelli, N.; Giorgi, R.; Fratini, E. B. P., 'Innovative method for the cleaning of water-sensitive artifacts: synthesis and application of highly retentive chemical hydrogels', *International Journal of Conservation Science* **4** (special issue) (2013) 715-722, [Article \(ijcs.ro\)](https://doi.org/10.1007/s10071-013-0001-0) (accessed 2024-07-25).
31. Pujari, J.; Pushpalatha, S.N.; Desai, P.D., 'Content-based image retrieval using color and shape descriptors', *International Conference on Signal and Image Processing*, Chennai, India (2010) 239-242, <https://doi.org/10.1109/ICSIP.2010.5697476>.
32. Kang, S.; Xing, B., 'Adsorption of dicarboxylic acids by clay minerals as examined by in situ ATR-FTIR and ex situ DRIFT', *Langmuir* **23**(13) (2007) 7024-7031, <https://doi.org/10.1021/la700543f>.
33. Kirwan, L. J.; Fawell, P. D.; van Bronswijk, W., 'In situ FTIR-ATR examination of poly (acrylic acid) adsorbed onto hematite at low pH', *Langmuir* **19**(14) (2003) 5802-5807, <https://doi.org/10.1021/la027012d>.
34. Kwak, H. S.; Lee, J. E.; Chang, Y. H., 'Structural characterisation of  $\beta$ -cyclodextrin crosslinked by adipic acid', *International journal of food science & technology* **46**(6) (2011) 1323-1328, <https://doi.org/10.1111/j.1365-2621.2011.02594.x>.
35. Mouanni, S.; Amitouche, D.; Mazari, T.; Rabia, C., 'Transition metal-substituted Keggin-type polyoxometalates as catalysts for adipic acid production', *Applied Petrochemical Research* **9** (2019) 67-75, <https://doi.org/10.1007/s13203-019-0226-0>.
36. Tomás Ferreira, J.; Damas, C.; Carita, M.; Correia, I.; van der Velde, E.; Verkens, K.; França de Sá, S., 'OH NO, NOT BLOOMING AGAIN! Assessing the influence of storage conditions in the reappearance of blooming on TPU coated fabrics', poster, in *Future Talks 023: Materials Matter. Cold and Current Cases in the Conservation of the Modern*, Munich (2023).

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