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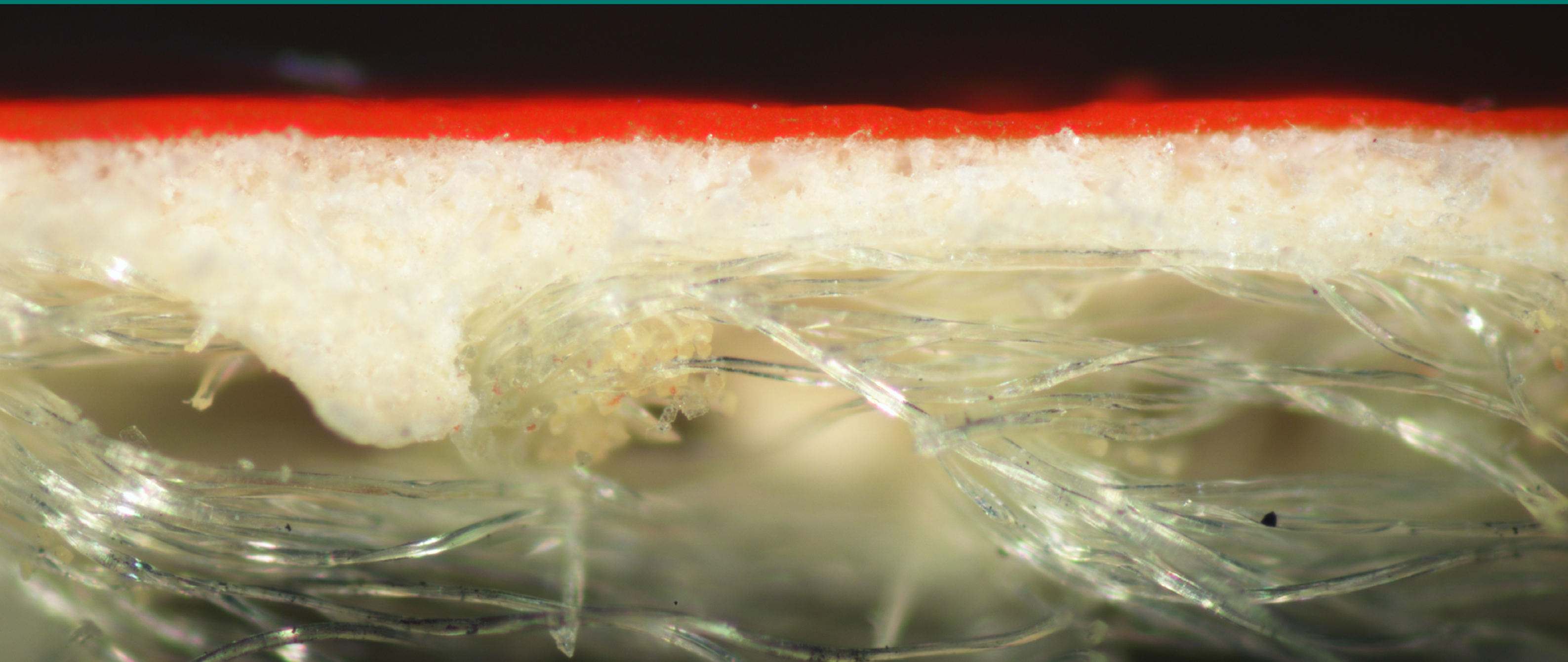
Synthetic-coated fabrics: challenges and conservation strategies
Tecidos revestidos por filmes sintéticos: desafios e estratégias de conservação

S. França de Sá, A. Rizzo, S. Scaturro, K. Verkens (Guest Editors | Editoras convidadas)



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CONSERVAR PATRIMÓNIO

EDITORIAL

Synthetic-coated fabrics: challenges and conservation strategies

Tecidos revestidos por filmes sintéticos: desafios e estratégias de conservação

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Synthetic-coated fabrics are composed of at least two layers: a textile or leather substrate, and a top coating made of a synthetic polymer. These coated fabrics are a large class of materials, with a huge variety of appearances, stratigraphies, and chemical compositions, for example: wet-, metal- or leather-look surfaces; and very simple or more complex stratigraphies that can include a top coating, adhesive layer, foam layer, and textile substrate. These fabrics are commonly found in fashion, design, and art collections, but also in technical, scientific, and industrial collections worldwide.

The goal of this issue is to advance and disseminate knowledge regarding the preservation and conservation challenges of synthetic-coated fabrics. Due to their complex, composite nature and susceptibility to decay – still scarcely explored in conservation literature – these materials present difficult and unprecedented challenges for conservators, curators, and scientists.

Only last year were these challenges acknowledged and tackled by a small group of institutional organisations and research project teams. Most importantly, from these initial efforts to address this subject many questions and urgent needs have emerged, launching future research horizons for the field.

One of those was the urgent need for more collaboration between the cultural heritage and industry sectors. This need was identified during the 2023 joint interim meeting organised by the ICOM-Committee for Conservation entitled "Semi-synthetic and synthetic textile materials in fashion, design and art", which proposed solutions and avenues of further research to address it. The popularity of the meeting with over 600 registrants attest to the urgency of this problem.

More recently, the symposium "Coated fabrics collection care" (May 2023), organized by the *Glossy Surfaces* project which was spearheaded by the ModeMuseum in Antwerp, Belgium, emphasized the urgent need for the development of successful treatment approaches. Although a niche focus, 110 participants attended this symposium, again emphasizing the need for further research.

The *Glossy Surfaces* project was the first of its kind to focus on the degradation and preservation of coated fabrics. The symposium convened at the end of the project revealed promising findings. First, it highlighted the large presence of polyurethane-based coatings in fashion collections worldwide, in opposition to p-PVC; second, it revealed blooming and flaking as the most urgent issues in conservation and restoration; and lastly, it presented findings on appropriate storage materials for the long-term preservation of TPU-coated fabrics.

Tackling these challenges demands a multidisciplinary approach, requiring collaboration amongst various experts and heritage professional care specialists, to link disparately-held knowledge between academia, industry, designers, and conservators.

This special issue contributes to filling this knowledge gap by gathering and presenting five studies dedicated to the safeguarding and conservation of synthetic-coated fabrics in cultural heritage. The contributions consider a variety of coating materials, bringing attention to the three most difficult to preserve (cellulose nitrate, polyurethane, and plasticised poly(vinyl chloride)); the wide range of artefacts (e.g. shoes, collars, and clothes); and one of the most important brands (Fabrikoid). It also includes insights into coated fabrics in *haute couture* (Gucci, Charles Jourdan) and ready-to wear fashion (e.g. Maria Gambina (PT), Valentina), thus illustrating the wide-range of synthetic-coated fabrics in heritage.

Topics include materials identification, the variance of coated fabrics stratigraphies, ageing characterisation by focusing on both polymer and volatile fractions, condition assessment strategies, and cleaning methodologies.

The paper by Neves et al. focuses on cellulose nitrate-coated fabrics, such as celluloid detachable collars and Fabrikoid artificial leather, highlighting the conservation challenges. Using advanced techniques like optical microscopy, μRaman and μFourier Transform Infrared spectroscopies, the research reveals that, while some cellulose nitrate-coated fabrics are well-preserved, others, especially those with castor oil, show significant degradation. This study aligns with historical degradation reports and calls for further research into the compatibility and reactivity of cellulose nitrate with various additives, to develop effective conservation strategies.

Van Rooijen et al. study addresses the off-gassing of volatile organic compounds (VOCs) from synthetic coatings, a critical concern for collection managers, as it signals ongoing degradation. Using Magic Chemisorbers and gas chromatography/ mass spectrometry (GC/MS), the study captures and analyzes VOCs emitted from plastic-coated textiles. Findings show that different coatings emit distinct compounds. This research elucidates degradation processes and demonstrates the efficacy of specific sorbents in monitoring and potentially mitigating these emissions, offering valuable insights into managing and preserving plastic-coated textiles.

Salinas and Ferraza's study focuses on coated fabrics in the high and ready-to-wear fashion industry. It compares TPU shoe coatings used by luxury and mass-production brands, revealing commonalities in materials and degradation issues. Using techniques like OM, SEM-EDX, and ATR-FTIR, the research provides a nuanced understanding of how both high-end and mass-market products face similar conservation challenges. These insights are crucial for developing tailored conservation approaches to address the specific needs of various types of synthetic-coated footwear.

Ferreira et al.'s investigation is likely the first comprehensive study on the stratigraphy of synthetic-coated fabrics. Using optical microscopy, the research examines the layer construction and morphology of p-PVC and TPU-coated fabrics. It uncovers subtle differences in production methods and delamination damages, offering a deeper understanding of material degradation factors. The insights gained are crucial for developing effective conservation strategies, highlighting the need for detailed material assessment and tailored preservation approaches for synthetic-coated textiles.

Finally, França de Sá et al. address the issue of blooming – a white deposit commonly found on aged TPU-coated fabrics – which presents a significant conservation challenge. The study explores preliminary methods for removing blooming, testing both dry and wet techniques, including the use of confined liquids in hydrogels. The research finds agar-agar to be the most effective medium for removing adipic acid deposits, though it acknowledges some limitations. This pioneering work offers a foundational approach for conservators aiming to mitigate blooming and preserve the aesthetic and historical value of TPU-coated fabrics.

The papers featured in this special issue collectively underscore the complexities and challenges associated with the conservation of synthetic-coated fabrics. By employing multi-analytical approaches and exploring conservation strategies, these studies provide a comprehensive understanding of the material properties, degradation processes, and effective preservation strategies for these invaluable artifacts.

As we continue to navigate the evolving landscape of contemporary textiles conservation, the insights and methodologies presented here will serve as a critical foundation for preserving the cultural heritage embodied in synthetic-coated fabrics.

Os tecidos revestidos por filmes sintéticos são compostos por pelo menos duas camadas: um substrato têxtil ou de pele, e um revestimento à base de um polímero sintético. Estes tecidos revestidos constituem uma grande classe de materiais, com uma enorme variedade de aparências, estratigrafias e composições químicas, por exemplo: superfícies muito brilhantes, metálicas ou semelhantes a pele; e estratigrafias muito simples ou mais complexas que podem incluir um revestimento no topo, uma camada adesiva, uma camada de espuma e um substrato têxtil. Estes tecidos são comummente encontrados em coleções de moda, design e arte, mas também em coleções tecnológicas, científicas e industriais em todo o mundo.

O objetivo deste número temático é avançar e divulgar o conhecimento sobre os desafios de preservação e conservação destes tecidos. Devido à sua natureza complexa e compósita, e suscetibilidade à deterioração, estes materiais apresentam desafios difíceis e sem precedentes para os conservadores, curadores e cientistas.

Somente no ano passado estes desafios foram reconhecidos e abordados por um pequeno grupo de organizações institucionais e equipas de projectos de investigação. Destes esforços iniciais surgiram muitas questões e necessidades urgentes, lançando horizontes de investigação futuros para esta área.

Uma das lacunas identificadas foi a necessidade urgente de mais colaboração entre os sectores do património cultural e da indústria. Esta necessidade foi identificada durante um encontro conjunto de 2023 organizado pelo ICOM-Comité para a Conservação, intitulado “Materiais têxteis semi-sintéticos e sintéticos em moda, design e arte”, que propuseram soluções e vias de investigação adicionais. A popularidade deste encontro com mais de 600 inscritos confirma a urgência deste problema.

Mais recentemente, o simpósio “Coated fabrics collection care” (Maio de 2023), organizado pelo projecto *Glossy Surfaces*, e coordenado pelo ModeMuseum em Antuérpia, Bélgica, sublinhou a necessidade urgente para o desenvolvimento de abordagens de tratamentos de conservação e restauro bem-sucedidas. Embora focado num tema mais específico, este simpósio contou com a presença de 110 participantes, sublinhando mais uma vez a necessidade de mais investigação.

O projeto *Glossy Surfaces* foi o primeiro a centrar-se na degradação e preservação de tecidos revestidos, e o simpósio realizado no final do projeto revelou resultados promissores. Em primeiro lugar, salientou a grande presença de revestimentos à base de poliuretano em colecções de moda em todo o mundo, em oposição ao p-PVC; em segundo lugar, revelou que as eflorescências brancas e a delaminação são questões urgentes a resolver nesta área; e, por último, apresentou resultados sobre os materiais de acondicionamento mais adequados para a preservação a longo prazo destes tecidos revestidos por TPU.

A resolução destes desafios exige uma abordagem multidisciplinar, que requer a colaboração entre vários especialistas e profissionais do do património cultural, para ligar conhecimentos díspares entre a academia, indústria, designers e conservadores.

Este número temático contribui para preencher esta lacuna no conhecimento, reunindo e apresentando cinco estudos dedicados à salvaguarda e conservação dos tecidos revestidos por filmes sintéticos no património cultural. As contribuições consideram uma variedade de materiais de revestimento, chamando a atenção para os três mais difíceis de preservar (nitrato de celulose, poliuretano e poli(cloreto de vinilo) plastificado); a vasta gama de artefactos (por exemplo, sapatos, golas e vestuário); e uma das marcas mais importantes (Fabrikoid). Inclui também informações sobre tecidos revestidos em alta costura (Gucci, Charles Jourdan) e em moda de pronto-a-vestir (por exemplo, Maria Gambina (PT), Valentina), ilustrando assim a vasta gama de tecidos revestidos sintéticos no património cultural.

Os tópicos incluem a identificação de materiais, a variabilidade estratigráfica dos tecidos revestidos, a caraterização do envelhecimento incluindo o estudo das fracções poliméricas e voláteis, a avaliação do estado de conservação e o estudo de metodologias de limpeza.

O artigo de Neves et al. centra-se nos tecidos revestidos por nitrato de celulose, como as golas destacáveis de celulóide e as imitações de pele Fabrikoid, salientando os desafios de conservação. Recorrendo a técnicas avançadas como a microscopia ótica e as microespectroscopias de Raman e de infravermelho por transformada de Fourier, a investigação revela que, enquanto alguns tecidos revestidos por nitrato de celulose estão bem preservados, outros, especialmente os que contêm óleo de rícino, apresentam uma degradação significativa. Este estudo está de acordo com relatórios históricos sobre a degradação deste material e apela a mais investigação sobre a compatibilidade e a reatividade do nitrato de celulose com vários aditivos, de forma a ser possível desenvolver estratégias de conservação mais eficazes.

O estudo de Van Rooijen et al. aborda a emissão de compostos orgânicos voláteis (VOC) a partir de revestimentos sintéticos, uma preocupação crítica para os gestores de colecções, uma vez que assinala a degradação em curso. Utilizando *Magic Chemisorbers* e cromatografia gasosa/espectrometria de massa (GC/MS), o estudo capta e analisa os VOC emitidos por têxteis revestidos por polímeros sintéticos. Os resultados mostram que diferentes revestimentos emitem compostos distintos. Esta investigação elucida os processos de degradação e demonstra a eficácia de adsorventes específicos na monitorização e potencialmente na mitigação destas emissões, oferecendo informações valiosas para a gestão e preservação de têxteis revestidos por estes filmes.

O estudo de Salinas e Ferraza centra-se em tecidos revestidos na indústria de moda de alta costura e de pronto a vestir. Compara os revestimentos de TPU para calçado utilizados por marcas de luxo e de produção em massa, revelando pontos comuns em termos dos materiais e dos problemas de degradação. Utilizando técnicas como microscopia óptica, SEM-EDX e ATR-FTIR, a investigação fornece uma compreensão pormenorizada da forma como os produtos de gama alta e de produção em massa enfrentam desafios de conservação semelhantes. Estes conhecimentos são cruciais para o desenvolvimento de abordagens de conservação adaptadas às necessidades específicas dos vários tipos de calçado com revestimentos sintéticos.

A investigação de Ferreira et al. é provavelmente o primeiro estudo abrangente sobre a estratigrafia de tecidos com revestimentos sintéticos. Utilizando microscopia ótica, a investigação examina a construção e a morfologia das diferentes camadas nos tecidos revestidos com p-PVC e TPU. Revela ainda as diferenças subtis nos métodos de produção e nos danos associados à delaminação, oferecendo uma compreensão mais profunda dos factores de degradação do material. Os conhecimentos adquiridos são cruciais para o desenvolvimento de estratégias de conservação eficazes, salientando a necessidade de uma avaliação pormenorizada dos materiais e de abordagens de preservação adaptadas aos têxteis com revestimentos sintéticos.

Por último, França de Sá et al. abordam a questão do blooming (eflorescências brancas) – um depósito branco comummente encontrado em tecidos envelhecidos com revestimentos de TPU – que representa um desafio de conservação significativo. O estudo explora métodos preliminares para remover estas eflorescências, testando métodos por via seca e via húmida, incluindo a utilização de líquidos confinados em hidrogéis. A investigação conclui que o ágar-ágar é o meio mais eficaz e seguro para remover estes depósitos de ácido adípico, embora reconheça algumas limitações. Este trabalho pioneiro oferece uma abordagem fundamental para os conservadores que pretendem atenuar as eflorescências e preservar o valor estético e histórico dos tecidos revestidos com TPU.

Os artigos apresentados neste número temático sublinham coletivamente as complexidades e os desafios associados à conservação dos tecidos revestidos por filmes sintéticos. Ao empregar abordagens multi-analíticas e ao explorar estratégias de conservação, estes estudos fornecem uma compreensão abrangente das propriedades do material, dos processos de degradação e das estratégias de preservação eficazes para estes artefactos de valor inestimável.

À medida que continuamos a navegar pelo cenário em evolução da conservação de têxteis contemporâneos, os conhecimentos e as metodologias aqui apresentados servirão como uma base crucial para preservar o património cultural incorporado nos tecidos revestidos por filmes sintéticos.

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The challenge of cellulose nitrate-coated fabrics: molecular characterization of celluloid detachable collars and Fabrikoid

O desafio dos tecidos revestidos com nitrato de celulose: caracterização molecular de colarinhos destacáveis de celulóide e Fabrikoid

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Abstract

In the 19th century, significant linen and leather imitation products were invented using cellulose nitrate-coated fabrics, including celluloid detachable collars and Fabrikoid artificial leather, now preserved in the Hagley Museum and Library, USA. Using optical microscopy, μRaman, and μFourier Transformed Infrared spectroscopies, this study highlights the need for characterizing the heterogeneity of these materials at the microscale. While the detachable collars have well-preserved fabric coatings composed of cellulose nitrate, camphor, anatase (TiO_2), and carbon-based particles, Fabrikoid's pigmented cellulose nitrate-castor oil systems show problems. Our molecular data align with a 1922 report on Fabrikoid degradation, revealing free fatty acids and carboxylates formed due to oil oxidation. This is concerning as these materials were used until the 1960s, demonstrated by the analysis of objects from the National Museum of Costumes in Portugal. Future studies should address the compatibility of cellulose nitrate with fatty acids and the reactivity of additives in these systems.

KEYWORDS
Cellulose nitrate
Castor oil
Coated fabrics
Material culture
Cultural heritage
Conservation

Resumo

No século XIX, foram desenvolvidas imitações de linho e couro utilizando tecidos revestidos com nitrato de celulose, como os colarinhos destacáveis de celulóide e o Fabrikoid, preservados no Hagley Museum and Library, EUA. Usando microscopia óptica e espectroscopias de Raman e infravermelho, este estudo destaca a necessidade de caracterizar a heterogeneidade destes materiais. Enquanto os colarinhos têm revestimentos bem preservados, compostos por nitrato de celulose, cânfora, anatase (TiO_2) e partículas à base de carbono, os sistemas de nitrato de celulose e óleo de rícino do Fabrikoid são problemáticos. Os dados moleculares revelaram a formação de ácidos gordos livres e carboxilatos devido à oxidação do óleo. Tal revela-se preocupante, pois a análise de objetos do Museu Nacional do Traje em Portugal demonstrou a utilização destes materiais até 1960. No futuro, a compatibilidade do nitrato de celulose com ácidos gordos e a reatividade de aditivos deve ser explorada em detalhe.

PALAVRAS-CHAVE
Nitrato de celulose
Óleo de rícino
Tecidos revestidos
Cultura material
Património cultural
Conservação

Introduction

Cellulose nitrate (CN) is a perennial challenge for the cultural heritage community. In the past 30 years, conservation scientists have studied cellulose nitrate degradation mechanisms in detail, which is fundamental to establishing efficient and sustainable conservation strategies [1-3]. However, cellulose nitrate degradation depends on the history of the multiscale heterogeneous systems composing cellulose nitrate artifacts. Due to the vast range of cellulose nitrate applications, the complete understanding of these historical systems is still limited. Degradation studies must comprehensively integrate different types of cellulose nitrate products and production methods, differing in formulations and processes, varying from factory to factory and country to country, allowing us to consider efficient conservation procedures tailored to each cellulose nitrate historical system.

Conservation studies have characterized a wide range of artworks from Naum Gabo, Antoine Pevsner, and László Moholy-Nagy; tridimensional celluloid objects, such as hand mirrors, combs, boxes, toothbrushes, piano keys, dentures, or billiard balls; photographic and cinematographic films; and lacquer/paint films [4-15].

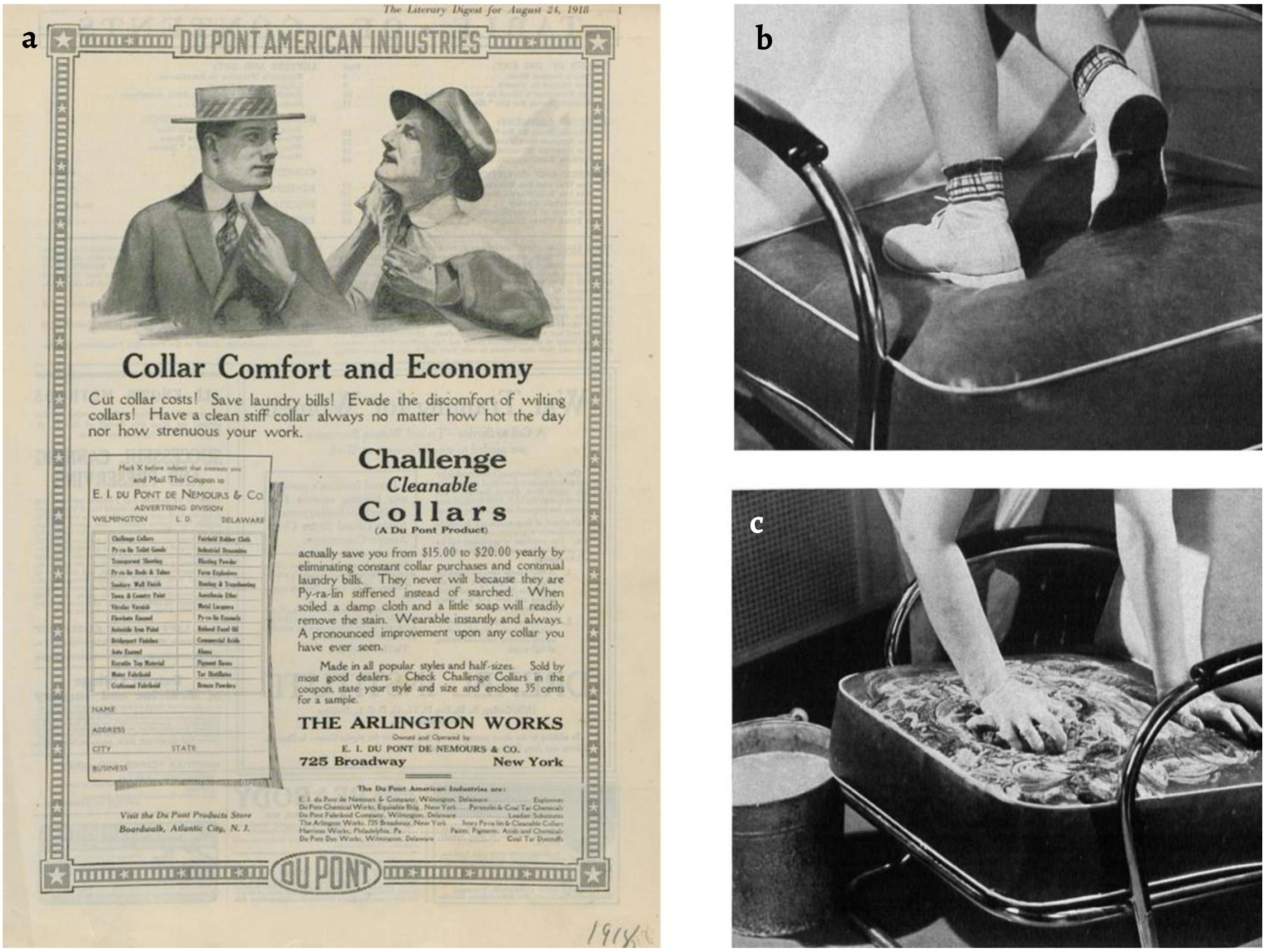
In comparison, this work emphasizes a small list of conservation studies focusing on cellulose nitrate-coated fabrics [16-17]. Ison et al.[16] identified an imitation leather upholstery of a nineteenth-century coach as a cellulose nitrate-coated fabric, stressing that "little is known about the use practices and composition of early coated fabrics found on actual historic objects" [16].

In 1855, Alexander Parkes patented the first process to coat fabrics with cellulose nitrate for waterproofing [18]. In the following decades, cellulose nitrate-coated fabrics led to the development of significant linen and leather substitutes, particularly celluloid, used for detachable collars and cuffs, and Fabrikoid, used to replace leather in a range of applications. This work aims to contribute to a better understanding of early coated fabrics by studying these two cellulose nitrate products. The following sections will briefly detail their production's historical significance and technical aspects.

Detachable celluloid collars

In the 1820s, the inconvenience and expense of laundering linen shirts led to the introduction of detachable collars and cuffs, permitting the separate cleaning and starching of these most exposed shirt parts. The growing middle class, particularly in the United States, found detachable collars an affordable way to maintain a clean appearance. However, while elegant, the detachable linen collars still required the worker to buy several pieces and to spend money on laundering and starching services, promoting the search for alternatives that were cost-competitive, durable, and easily cleaned at home [19-20].

Experiments to apply cellulose nitrate as a waterproof coating started in the late 1850s by covering the surface of the cloth with collodion or by casting a thin cellulose nitrate film over a glass and, when nearly dry, adhering it to the cloth. However, these methods did not allow a smooth and even finish. Only with the invention of celluloid sheets by John W. Hyatt in the 1870s was it possible to achieve the technical requirements, such as strength, stiffness, flexibility, color, and regularity, needed to create a viable alternative to all-linen collars [18]. Rufus Sanborn, Albert Sanborn, and Charles Kanouse were the first to use celluloid sheets to manufacture collars and cuffs in 1878. Their method was deceptively simple: a sheet of muslin or linen was placed between two sheets of celluloid, and pressure was applied to unite the three layers, achieving a stiff and easily cleaned linen imitation [21].



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(A Du Pont Product)

actually save you from $15.00 to $20.00 yearly by eliminating constant collar purchases and continual laundry bills. They never wilt because they are Py-ra-lin stiffened instead of starched. When soiled a damp cloth and a little soap will readily remove the stain. Wearable instantly and always. A pronounced improvement upon any collar you have ever seen.

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Figure 1. Cleaning advertisements: *a)* 1918 advertisement for the "Challenge Cleanable Collars" focusing on the economy advantages of having an easily cleanable material; *b-c)* from Du Pont Magazine (1938) showing how easily Fabrikoid could be cleaned with soap and water. Cleaning operations like these raise conservation questions regarding their impact in material lifetime (images: Hagley Museum and Library).

Detachable celluloid collars and cuffs offered practicality and ease of care. They were used by a wide range of workers, from police officers to clerks. Due to celluloid's imitative nature, many consumers deemed celluloid collars inelegant and associated them with naïve country rustics or social climbers. Therefore, the celluloid collar and cuff had a smaller market size than linen. However, it was active enough to support manufacturing by celluloid companies such as the American Arlington Manufacturing Company or the British Xylonite Company [19]. The Arlington Mfg. Co. was established in 1885 in New Jersey and labeled their celluloid plastic "pyralin". In 1915, the company was purchased by E. I. du Pont de Nemours and Company, which started advertising their "new" pyralin collars – the "Challenge cleanable collars" (Figure 1). Production continued until 1939, using the Sanborn-Kanouse method of layering cotton fabric between cellulose nitrate plastic sheets [22].

By the 1920s, stiff collars started to wane due to the more relaxed fashion trends. With the advancements in washing machines and fabric technology, buying, and washing entire shirts became a realistic and cost-effective choice for the average consumer [23-24]. Today, detachable celluloid collars can be found in notable collections, including those at the Smithsonian Institution (USA), the Museum of Design in Plastics (UK), and the Deutsches Kunststoff Museum (Germany). These collars symbolize an era when male dress codes required stiff, impeccably white collars, showcasing the ingenuity of the early inventors of semisynthetic coated fabrics in tackling market needs imposed by nineteenth-century social inequalities.

The whiteness of the celluloid detachable collars

The whiteness of the celluloid collars and cuffs was crucial for its commercial success. Worden [18] states that zinc and manganese salts were used, although zinc and manganese carbonates were avoided because they would turn yellow by reacting with the sulfur released during perspiration. He added that high quantities of zinc and manganese salts would decrease the waterproofing properties due to increased porosity. Waterproofing was essential for the easy cleaning procedures, but the lower the quantity of white pigment, the lower the whiteness strength of the final product. To increase the white appearance of the finished product, J. W. Hyatt added an inner blue tint backing to the celluloid sheets.

DuPont formed the Krebs Pigment and Color Corporation to make titanium dioxide (TiO_2) pigment in 1931. There are two processes to make TiO_2 pigments: sulfate and chloride. Both processes can produce rutile pigment, while anatase pigment can solely be derived from the sulfate process. Until 1941, Dupont used the sulfate process to produce anatase. Afterward, the company started producing rutile pigment due to its higher opacity and tinting strength; rutile has a refractive index of 2.72, the highest of any white pigment; anatase has a refractive index of 2.54 and zinc oxide of 2.0 [25].

Fabrikoid

As for celluloid detachable collars, the development of cellulose nitrate artificial leather derived from the interest in enhancing the properties of natural fabrics, rendering them more durable, waterproof, easily washable, or immune to biological attack. According to Worden [18], the Englishmen Wilson and Story developed the standard formula for producing successful cellulose nitrate artificial leather in 1884. The method involved coating the cloth with cellulose nitrate, amyl acetate, and castor oil.

Castor oil is primarily composed of ricinoleic acid (>89 %) and other fatty acids such as linoleic (4 %), oleic (3 %), stearic (1 %), and palmitic acids (1 %). Due to castor oil's non-volatile, non-drying, and solubility characteristics (soluble in alcohols in any proportion), it was extensively tested in combination with cellulose nitrate to increase the flexibility of the final products [26]. Depending on the desired flexibility, the amount of castor oil in the mixture could be increased to match cellulose nitrate [27].

A pioneering American company in producing cellulose nitrate artificial leather at a large scale was the Pegamoid Company, established in 1895 in Hohokus, New Jersey. In 1900, the factory plant moved to Newburgh, New York, and the company was renamed The Fabrikoid Company. In 1910, E. I. du Pont de Nemours and Company strategically acquired the Fabrikoid Company during a crucial juncture in its trajectory, marked by its initiative to diversify its market presence beyond explosive products [28].

In the 1920s, the formulation of Fabrikoid closely resembled that of Wilson and Story:

1) cellulose nitrate (with an average degree of substitution of 2.1) was dissolved in an organic solvent (a mixture of amyl acetate, ethanol, and benzene) to create a cellulose nitrate "jelly" or "dope";
2) pure castor oil was blended with the desired pigments and added to the dope;
3) the dope was spread uniformly onto a fabric (described as greige or "grey" goods), previously dyed to match the color of the dope, employing a specially-designed-coating machine called "doctor-knife";
4) after applying a specific number of coats, determined by the end-use of the product, the roll of coated fabric underwent pressure (10^4 pounds per square inch) to consolidate the layers of dope, smoothen the surface, and achieve the desired artificial leather texture. [29]

As Meikle [30] explained, the manufacturing process of Fabrikoid was "mechanized, virtually automated, and continuous". The mechanization of Fabrikoid led to reduced production costs and faster manufacturing compared to the traditional, labor-intensive leather industry, making it an affordable and readily accessible material. It was produced in rolls ranging from 25 to 50 meters long, with uniform thickness, appearance, and quality. In addition, the possibility of cleaning operations with aqueous solutions was an advantage (Figure 1). Fabrikoid was used in various applications, mainly in the automobile industry, but also in furniture, footwear, luggage, wall coverings, or bookbinding. In such novel objects as cameras and portable phonographs, no cultural norms dictated the need for leather-like surfaces. The innovative use of Fabrikoid in such objects suggests its influence in creating a modern world of artificial surfaces and textures.

The degradation of Fabrikoid

The formulation of Fabrikoid was inherently unstable due to the combination of cellulose nitrate with high concentrations of castor oil. Discussions on formulation problems due to high concentrations of castor oil are well-known in the history of cellulose nitrate plastics. For example, it is conjectured to have been Alexander Parkes's greatest technical error in making Parkesine, the first cellulose nitrate plastic. Du Pont carried out intensive laboratory research to understand and prevent the degradation of Fabrikoid, which they reported in 1922 [31]. The report was divided into two parts: A) the causes of rancidity, tackiness, and brittleness, and B) the study of oxidation inhibitors. The results of this research concerning the rancidity tests are relevant for the conservation field, and the main results are summarized in Table 1.

The first stage of Fabrikoid degradation was rancidity development, i.e., oil oxidation. Rancidity induced an “offensive odor” due to the production of shorter carbon chain fatty acids. This issue was particularly problematic for indoor uses. The prominent factors influencing the rancidity rate were the pre-processing and acidity of the oil (free fatty acids), the cellulose nitrate quality, the pigments, and the storage conditions. Rancidity tests of castor oil with an acidity ranging from 1 % to 93.4 % showed that the higher the acidity, the faster the rancidity rate. Mixtures with “high stability” CN took more time to turn rancid, likely meaning CN of low impurity content, such as residual sulfate groups, which are known to accelerate CN degradation [32]. Fabrikoid samples exposed to light at room temperature, particularly wavelengths below 400 nm, degraded faster when compared with thermal degradation (65 °C) in dark conditions. It is known that the cellulose nitrate mechanism of photodegradation is identical to thermal degradation, with a faster oxidation rate [2].

Carbon-based materials had a strong retarding effect on rancidity due to their acid and moisture adsorbent properties. Several oxidation inhibitors were tested with 2-aminophenol, tannic and gallic acids being the most efficient. Overall, the oxidation inhibitors were more efficient under dark conditions, Table 1. For economic reasons, a 1 % w/w concentration of tannic acid was chosen for industrial use in all products except those with light colors since all aromatic compounds led to discoloration in white goods.

The second stage of Fabrikoid degradation was tackiness due to the exudation of the fatty acids. Du Pont’s report proposed that shorter carbon chain fatty acids had higher solvation power over cellulose nitrate, forming a tacky superficial layer. However, no data was provided, for example, glass transition temperature (T_g). The last stage – brittleness – was only observed in white goods due to the presence of zinc oxide and the formation of zinc soaps. The reactivity of zinc oxide in oil-based paintings has been thoroughly studied due to the consequential cracking and delamination arising from saponification. In these systems, zinc oxide reactivity depends on several factors, such as the properties of the pigment, oil, and environmental factors [33]. To the author´s knowledge, no studies have yet been performed to understand the hydrolysis and saponification mechanisms in cellulose nitrate–castor oil-based systems.

Table 1. Fabrikoid rancidity tests reported by Du Pont in 1922 [31]. An increase in the number of days to rancidity indicates greater efficiency of the additive's stabilizing action.

Additive		**% w/w in CN-castor oil film**	**Rancidity / days**[*]	
			65 °C	**Window**
Oxidation Inhibitors	2-aminophenol	0.375	180	-
	Tannic acid	"	120	90
	Gallic acid	"	120	-
	Pyrogallol	"	102	70
	Phloroglucinol	"	75	63
	Picric acid	3	65	32
	Beta-naphthol	0.375	64	-
	Citric acid	"	11	-
Adsorbent	Alumina hydrate	4	6	46
	Bone-black	4	35	60
		0.5	3	35
	Activated charcoal	0.5	3	35
Pigments	Bone black	16.6	210	100
	Van Dyke brown	"	180	-
	Lake pigments	"	60-65	95
	Yellow ochre (Fe_2O_3, SiO_2)	"	5	52
	Ultramarine blue	"	3	39
	Red oxide (Fe_2O_3)	"	2	45
	Chrome yellow ($PbCrO_4$)	"	2	24
	Burnt siena (Fe_2O_3, Al_2O_3)	"	2	24
	Zinc oxide	"	2	9
	Prussian blue	"	1	7
	Lithopone ($ZnS + BaSO_4$)	"	1	7
	Raw umber (Fe_2O_3, MnO_2)	"	1	7

[*] Rancidity was detected by odor. Two aging methods were employed: thermal aging at 65 °C; and photoaging (sunlight) in a sealed glass container at room temperature.

Research aims

The main aim of this study was to analyze the formulations utilized in celluloid detachable collars and Fabrikoid. To achieve this, we examined three case studies from the Hagley Museum and Library collection using μRaman and μFTIR spectroscopies: two cleanable detachable collars and a marketing brochure of Fabrikoid consisting of nine sheets in various colors (Figure 2).

For the collars, our objective was to confirm the composition of the coating, typically a blend of cellulose nitrate and camphor, and to identify any additional additives present. According to Worden [18], castor oil was commonly added to celluloid collars in 15-20 % ratio by weight to "give a slight feeling of pliability". Considering the concerns about the stability of cellulose nitrate-castor oil systems, it was important to ascertain the presence of castor oil. Another crucial aspect was the identification of pigments used, such as zinc oxide or titanium oxide (rutile or anatase), or others. In cellulose nitrate-camphor systems (without oils), zinc oxide serves as a stabilizer with UV-absorbing and acid-neutralizing properties [32]. However, Du Pont's 1922 report on Fabrikoid degradation indicated that when castor oil is combined with cellulose nitrate, the reactivity of zinc oxide can be detrimental to the system. Pigments also play a role in dating the objects, particularly considering Du Pont's advancements in titanium oxide technology since 1931. Titanium dioxide pigments have higher refractive indices than zinc oxide, which is pertinent for applications requiring a white color, such as collars.

COLOR

For identification of colors above, lift the tip of each swatch
All samples 6200 Armor, 0-7 Grain
FM-426 finish, soft pliability.

THERE is no mystery in color. Authorities may differ on how color should be applied or handled, but they all work from the spectrum—the spectrum which is as old as the world we live in. We are definitely not concerned here in these pages with color principles or systems because such information is already available from recognized authorities on the scientific application of color.

For a number of years, however, we have made a careful and continuing analysis of color trends or preferences based on actual sales of 6200 Armor Quality "Fabrikoid" throughout the world. Confronted with the task of building and maintaining finished stocks from which prompt deliveries can be made to our customers, we stock only colors that sell. We have a sample book showing the various grain, finish, and color combinations which we stock in 6200 Armor Quality "Fabrikoid" for upholstery. If you have a color problem in upholstery, this book is yours for the asking.

DU PONT
REG. U.S. PAT. OFF.

E. I. DU PONT DE NEMOURS & CO. (INC.)
"FABRIKOID" DIVISION
NEWBURGH, NEW YORK

Figure 2. Three objects from the Hagley Museum and Library collection studied: *a)* challenge cleanable collar, puritan style, "collar A"; *b)* pyralin cleanable collar, Aberdeen style, "collar B"; *c)* "6200 Armor Quality" Fabrikoid brochure with nine sheets of different colors where it is possible to see the overall whitish surface deposit.

The Fabrikoid set was an opportunity to understand better the complexity of cellulose nitrate-castor oil systems and their degradation issues. The Fabrikoid sheets, covered with Melinex sheets, exhibited blooming characterized by a whitish surface deposit (Figure 2). This study sought to gain insight into the underlying degradation mechanism responsible for this observed blooming by combining molecular data of the base formulation and pigments employed in each sheet with technical information collected from the 1922 DuPont report. Furthermore, considering the probable post-1922 manufacture date of the Fabrikoid set relative to the DuPont report, the composition of these sheets offers a preliminary exploration of the potential industrial-scale ramifications of DuPont's experiments.

Lastly, to assess the presence of cellulose nitrate-coated fabrics in Portuguese cultural heritage collections, we selected four objects from the National Museum of Costumes in Portugal (Museu Nacional do Traje) dating from the 1920s to the 1960s, which contained artificial leathers vaguely described as "nappa" in their compositions (in Portuguese the word "napa" is commonly used for artificial leathers).

Experimental

Detachable celluloid collars from the Hagley Museum and Library

In this work, two detachable collars from the Hagley Museum and Library were analyzed by µFTIR and Raman. Both collars are in good conservation condition. "Collar A" is a Challenge cleanable collar, puritan style, and size 15 ½ (inventory number 69.46.213). Advertisement for this type of collar was found in a 1919 Du Pont catalog, sold at 35c each. “Collar B” is a pyralin cleanable collar, Aberdeen style and size 15 ½ (inventory number 69.462.295) (Figure 2). C.E. Buckley Co., Leominster, Massachusetts, produced both collars. On April 6, 1939, C.E. Buckley Co. purchased Du Pont’s collars and cuffs departments [34]. This year, they started producing Challenge, Blue Ribbon, and Water Nymph collars for "clergymen, businessmen, postmen, soldiers, naval officers, workmen, railroad employees, nurses, nuns, waiters, orchestra musicians". This company continued to manufacture these products for years to come. In 1974, the collars were only marketed as clerical, showing the commercial tapering of this accessory towards this profession.

Fabrikoid samples from the Hagley Museum and Library

The “6200 Armor Quality” Fabrikoid brochure with nine sheets of different colors was found in the E.I. du Pont de Nemours & Company, Advertising Department records 1803, box 40. The Fabrikoid sheets were covered with a Melinex sheet and showed a whitish surface deposit. Part of the surface deposit was adhered to the Melinex when it was removed. This brochure was undated. However, there are records advertising this product from 1925 to 1946. This Fabrikoid type was mainly marketed for upholstery but also found application in book bindings. Sheet 9 was not sampled due to storage limitations (Figure 2).

Samples from the National Museum of Costumes, Portugal

As the National Museum of Costumes in Portugal lacked any items classified as containing Fabrikoid or any other cellulose nitrate-coated fabric, the search focused on the keyword “nappa” and dates between 1920 and 1960. Ultimately, four objects were chosen for examination, described in “Results and discussion” section.

Materials

The following materials were used as Raman and infrared material references: pure cellulose nitrate membranes (Amersham Protran, 0.2 µm), camphor (96 %, Sigma-Aldrich), pure microcrystalline cellulose powder (Sigma-Aldrich), pure castor oil (Soft & Co), barium sulfate (99 %, Alfa Aesar), palmitic acid (98 %, Panreac) and zinc palmitate [35].

Equipments

Optical microscoy (OM)

Micrographs were acquired using an Axioplan 2ie Imaging system (Zeiss, Germany) equipped with an incident halogen (tungsten-halogen light source, HAL 100) and UV radiation (mercury light source, HBO 100) illuminators and coupled with a DXM1200F digital camera and ACT-1 control software (Nikon, Japan). The samples were analyzed using ocular lenses with a magnification of 10× and Epiplan objective lenses with magnifications of 20× and 50× for a total optical magnification of 200× and 500×, respectively. The scales for all objectives were calibrated within the Nikon ACT-1 control software. Fluorescence microscopy images were acquired with ultraviolet light (Zeiss Filter set 02 – excitation G 365 nm, beamsplitter FT 395 nm, emission LP 420 nm).

Micro Fourier transformed infrared spectroscopy (µFTIR)

The micro samples were acquired under a ZEISS stereomicroscope using TED-Pella microtools. Under the microscope, it was observed that the collar was composed of two coating layers and an interior composed of threads of fabric. Samples were acquired from both regions. The micro samples acquired were analyzed with micro-Fourier on a Nicolet iS50 FT-IR spectrophotometer equipped with a Nicolet Continuµm (15× objective) microscope and a Mercury – Cadmium – Tellurium (MCT) detector cooled by liquid nitrogen. Micro samples were placed on a DC-3 diamond compression cell (Specac), and the spectra were acquired in transmission mode between the 4000-650 cm⁻¹, with a resolution of 8 cm⁻¹ and 254 scans. For the quantification of cellulose nitrate degree of substitution (DS) and the proportion of camphor (% w/w) in a celluloid object, were applied the infrared calibration curves developed by Neves et al. [10]. Briefly, DS is an indicator of molecular degradation since it decreases with CN heterolytic hydrolysis induced by light, heat, or moisture; and camphor concentrations tend to decrease over time due to sublimation. Carbonyl band areas were measured using OMNIC "peak area tool".

Micro Raman spectroscopy (µRaman)

Micro-Raman spectra were collected on a Labram 300 Jobin Yvon spectrometer equipped with a He-Ne laser (632.8 nm, 17 mW) and a diode laser (785 nm, 100 mW). The laser beam was focused with an Olympus 100× lens with a spot size of 2 µm. The conditions used are provided for each spectrum.

Results and discussion

Detachable celluloid collars

The infrared spectra of both celluloid collars showed that the white coating is composed of celluloid (cellulose nitrate and camphor) and the inner fabric is composed of a cellulosic fabric. In more detail, cellulose nitrate was identified by its characteristic infrared nitrate group stretching bands at 1650 ($\nu_a NO_2$), 1280 (νNO_2) and 844 (νNO) cm^{-1} and the cellulosic acetal structure between 1200 and 900 cm^{-1}. Camphor was identified by the carbonyl stretching vibration at 1731 cm^{-1} and CH stretching and bending vibrations between 3000-2800 cm^{-1} and 1500-1300 cm^{-1}, respectively [36] (Figure 3). There were no spectral features that indicated the presence of castor oil in the formulation.

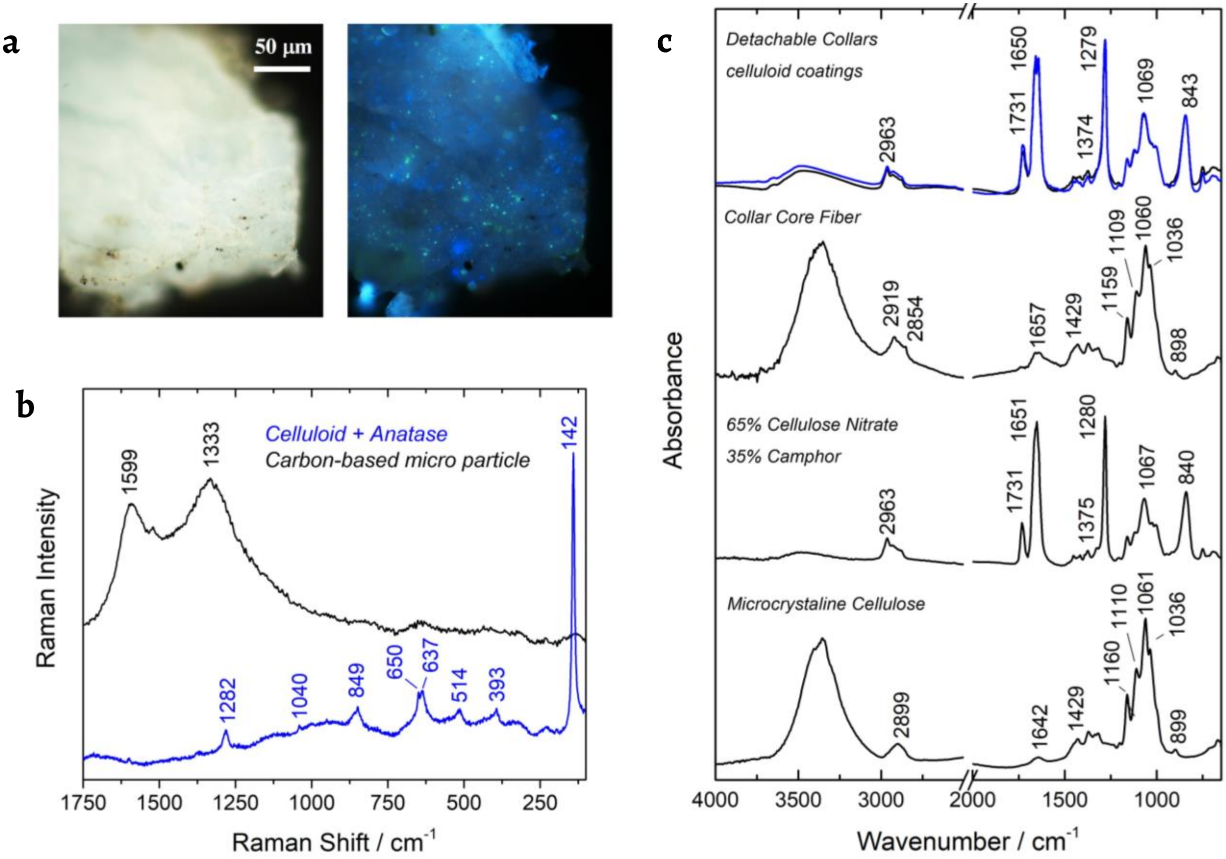


Figure 3. "Collar A": *a-b)* Micrographs (500×) of a microsample observed under cross-polarized light and with UV light (λ_{exc} = 365 nm); *c)* Raman spectra (633 nm laser) of anatase (TiO_2, 120 s acquisition time, 3 cycles) and of a carbon-based particle (60 s acquisition time, 1 cycle); *d)* Infrared spectra of the detachable collars' white celluloid coatings and inner cellulosic fabric fiber compared with references of pure celluloid (65 % cellulose nitrate and 35 % camphor) and microcrystalline cellulose.

The average degree of substitution (DS) of cellulose nitrate and the proportion of camphor (% w/w) were quantified: DS 1.78 (± 0.06) and 27 % w/w (± 2) camphor for collar A; and DS 1.85 (± 0.08) and 33 % w/w (± 1) camphor for collar B. This molecular information shows the collars' aging, with the DS being lower than stated by the literature for the DS used in manufacture (DS 2.1). The concentration of camphor continues to be high for both collars, with lower concentration correlating with lower average DS.

Surprisingly, under the microscope using cross-polarized light, it was possible to observe dark micrometer particles dispersed in the white matrix. μRaman analysis showed that these particles are composed of a carbon-based material by the detection of graphite D and G vibration bands at 1333 and 1599 cm^{-1}, respectively [37] (Figure 3). Based on the findings reported in 1922, it is possible that this carbon-based material was used in low concentrations for stabilization purposes.

The Raman spectra acquired for the collars showed that the pigment used was anatase (TiO_2), by the observation of characteristic O-Ti-O bond bending vibrations at 141 (E_g) and 396 (B_{1g}) cm^{-1} and the Ti-O stretching vibrations at 512 (A_{1g}) and 637 (E_g) cm^{-1} [38]. No other white material was found. The luminescence observed in collar A insights into the heterogeneity of anatase–celluloid systems. The bandgap for anatase is 3.2 eV (387 nm) and its emission depends on intrinsic defects; for example, green emissions arise from "intra-bandgap states associated with oxygen vacancies" [39] (Figure 3). The presence of anatase in both collars suggests a date for these objects between 1939 and 1941; C.E. Buckley Co. only started manufacturing collars in 1939 and Du Pont shifted to the production of rutile in 1941.

The inner fabric material is composed of cellulose fibers identified by the characteristic acetal structure bands in the region between 1250 and 900 cm^{-1} and the strong absorption in the OH region 3500-3000 cm^{-1}, comparable with the pure microcrystalline cellulose infrared spectrum (Figure 3). The additional bands observed at 2919 and 2854 cm^{-1} related to CH stretching vibrations, in combination with a weak band at 1739 cm^{-1} due to carbonyl group stretching, is suggestive of traces of a wax or resin [40].

Fabrikoid

All Fabrikoid sheets showed similar infrared spectra, confirming their common cellulose nitrate–castor oil-based composition. Interestingly, another shared compound found was barium sulfate ($BaSO_4$) (Figure 4, Figure 5 and Table 2). Using infrared spectroscopy, cellulose nitrate was identified by characteristic nitrate group stretching bands at circa 1650 ($\nu_a NO_2$), 1280 (νNO_2) and 840 (νNO) cm^{-1}. Castor oil bands were characterized by the CH and CH_2 stretching vibrations observed at circa 2925 and 2855 cm^{-1} and CH_3 asymmetric bending at circa 1460 cm^{-1}. Shifts in the CH vibrations positions can be due to oxidation or to the interaction of the oil with the pigments [41]. Barium sulfate was identified by its characteristic sulfate group (SO_4) triply degenerate vibrational modes (ν_3) at 1180, 1120 and 1080 cm^{-1} [42]. Shifts observed in these vibration bands are due to changes in concentration. In Figure 4, an infrared spectral sum of CN, castor oil and $BaSO_4$ reference spectra (1:1:1 proportion) is compared with Fabrikoid sheet number 1 infrared spectrum, supporting the presence of this three-component system in all sheets. μRaman supported the identification of $BaSO_4$ by the observation of the strong SO_4 symmetric stretching at 986 cm^{-1}, asymmetric bending at 615 cm^{-1} and asymmetric bending modes at 458 and 450 cm^{-1} [43] (Table 2).

The increase of the area of the carbonyl band is related to the oil oxidation: unaged castor oil carbonyl area = 8.2 vs average carbonyl area in Fabrikoid sheets = 11.2 (normalized) [44]. The shift of the maximum to lower wavenumbers is related to the formation of saturated free fatty acids. This was confirmed by the detection of the infrared characteristic bands of palmitic acid when analyzing the whitish deposit at the surface of the Fabrikoid sheets (Figure 4). This fatty acid is one of the primary oxidation products of unsaturated C18 fatty acids, together with stearic and azelaic acids [33]. Infrared vibration bands found in sheets 3, 5 and 6 at 1539 cm^{-1}

suggested the presence of metal carboxylates, namely zinc palmitate and stearate. This was confirmed by μRaman that detected peaks related to zinc carboxylates [35] (Figure 4).

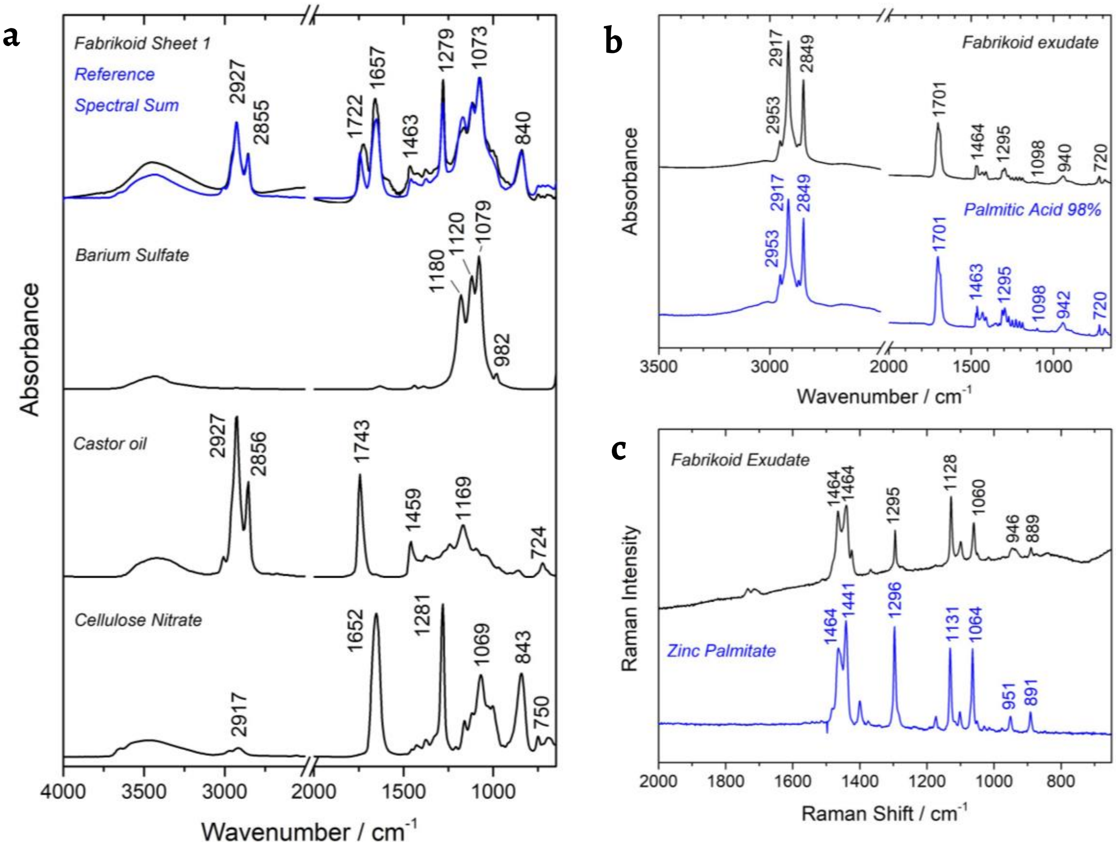


Figure 4. Infrared spectrum of the: *a)* Fabrikoid brochure sheet 1, compared with a spectral sum (proportion 1:1:1) of the reference infrared spectra showed below, namely barium sulfate ($BaSO_4$), castor oil and cellulose nitrate; *b)* Fabrikoid exudate (removed from the Melinex sheet) compared to a reference infrared spectrum of palmitic acid (98 %); *c)* Raman spectrum of the Fabrikoid exudate in sheet 6 compared to a reference infrared spectrum of zinc palmitate (633 nm laser, 17 mW, 60 s, 3 cycles).

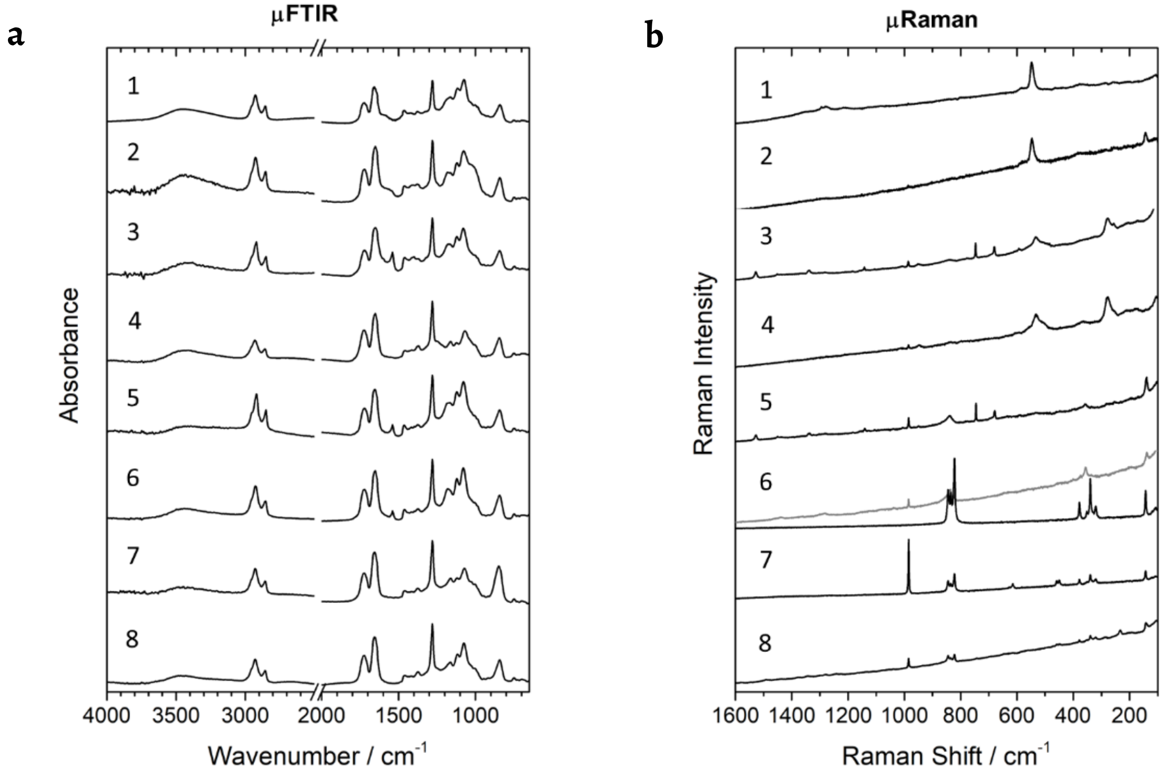
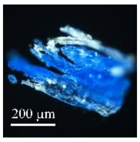
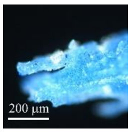
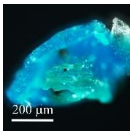
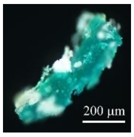
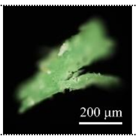
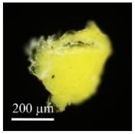
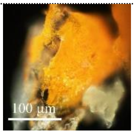
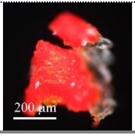


Figure 5. Spectra of the Fabrikoid sheets: *a)* Infrared and *b)* Raman (785 nm laser, 100 mW, 5-50 s acquisition time, 1-5 cycles). For μRaman analysis of sheet 8, a density filter was used (10 mW) due to intense fluorescence background, probably from an organic red pigment.

Table 2. Characterization of the Fabrikoid sheets (cross-polarized light micrographs, µInfrared and µRaman results). Molecular vibrations and associated literature are provided for each compound.

Sheet number	OM	µFTIR / cm^{-1}	µRaman / cm^{-1}
1		Cellulose Nitrate: 1654 ($\nu_a NO_2$), 1280 (νNO_2), 842 (νNO) [36] Castor oil: 2928, 2856 (νCH_2), 1460 (νCH_3) [41] Barium Sulfate: 1165, 1121, 1078 ($\nu_3 SO_4^{2-}$) [42]	Ultramarine Blue: 548 (ν_s S^{3-}), 581sh [45]
2		Cellulose Nitrate: 1651, 1280, 841, 750 Castor oil: 2926, 2854, 1461 Barium Sulfate: 1182, 1121, 1077	Ultramarine Blue: 548, 581sh Anatase: 144 (δO-Ti-O) [38] Barium Sulfate: 986 (δ_a SO_4^{2-}) [42]
3		Cellulose Nitrate: 1652, 1280, 842 Castor oil: 2924, 2854, 1452 Barium Sulfate: 1179, 1121, 1078 Prussian Blue: 2086 ($\nu C{\equiv}N$) [46] Zinc Carboxylate: 1539 ($\nu_{as} COO^-$) [35]	Green Earth: broad peaks at 277 and 532 (possibly glauconite) [47] Phthalocyanine blue: 1526, 1451, 1337, 746, 680 [48] Barium Sulfate: 986 cm
4		Cellulose Nitrate: 1654, 1281, 844 Castor oil: 2930, 2858, 1457	Green Earth: broad peaks at 277 and 532 (possibly glauconite) Barium Sulfate: 986
5		Cellulose Nitrate: 1654, 1280, 842 Castor oil: 2928, 2856, 1460 Barium Sulfate: 1165, 1121, 1078 Zinc Carboxylate: 1539	Phthalocyanine blue: 1526, 1451, 1337, 746, 680 Chrome Yellow: 837 (ν_a CrO_4^{2-}), 359 (ν_s CrO_4^{2-}) [49] Barium Sulfate: 986
6		Cellulose Nitrate: 1651, 1373, 1280, 843 Castor oil: 2926, 2855, 1461 Barium Sulfate: 1180, 1120, 1079 Zinc Carboxylate: 1539	Chrome Yellow: 837 (ν_a CrO_4^{2-}), 359 (ν_s CrO_4^{2-}) Chrome Orange: 845, 836, 822, 378, 351, 339, 320 [50] Barium Sulfate: 986
7		Cellulose Nitrate: 1657, 1280, 848 Castor oil: 2928, 2856, 1459 Barium Sulfate: 1161, 1120, 1072	Chrome Orange: 845, 836, 822, 378, 351, 339, 320 Anatase: 143 (δO-Ti-O) Barium Sulfate: 986, 615 (δ_a SO_4^{2-}), 458 and 450 ($\delta_s SO_4^{2-}$) [42]
8		Cellulose Nitrate: 1656, 1280, 842 Castor oil: 2928, 2857, 1459 Barium Sulfate: 1163, 1115, 1074	Chrome Orange: 845, 836, 822, 378, 351, 339, 320 Anatase: 142 (δO-Ti-O) Barium Sulfate: 986, 458, 450

The list of pigments that give color to the Fabrikoid sheets is shown in Table 2. Two pigments reported in 1922 to accelerate degradation were found in Fabrikoid sheets 3, 5 and 6: Prussian Blue ($Fe_4[Fe(CN)_6]_3$) and Chrome Yellow ($PbCrO_4$). Interestingly, infrared bands related to zinc carboxylates were only observed for the sheets where these pigments were found. It is relevant to observe that zinc oxide (ZnO) was not detected. The only white pigment identified was anatase (TiO_2).

Samples from the National Museum of Costumes in Portugal

The µFTIR and µRaman analysis of the coatings collected from the National Museum of Costumes underline the diversity of cellulose nitrate-oil formulations that can be found in cultural heritage collections (Table 3 and Figure 6). It was possible to observe the presence of three different fillers: barium sulfate ($BaSO_4$), calcium carbonate ($CaCO_3$) and calcium sulfate (gypsum, $CaSO_4$). The colorants found were the same for the Fabrikoid set, with the additional identification of iron (III) oxide (Fe_2O_3), also mentioned in the DuPont 1922 report (Table 1).

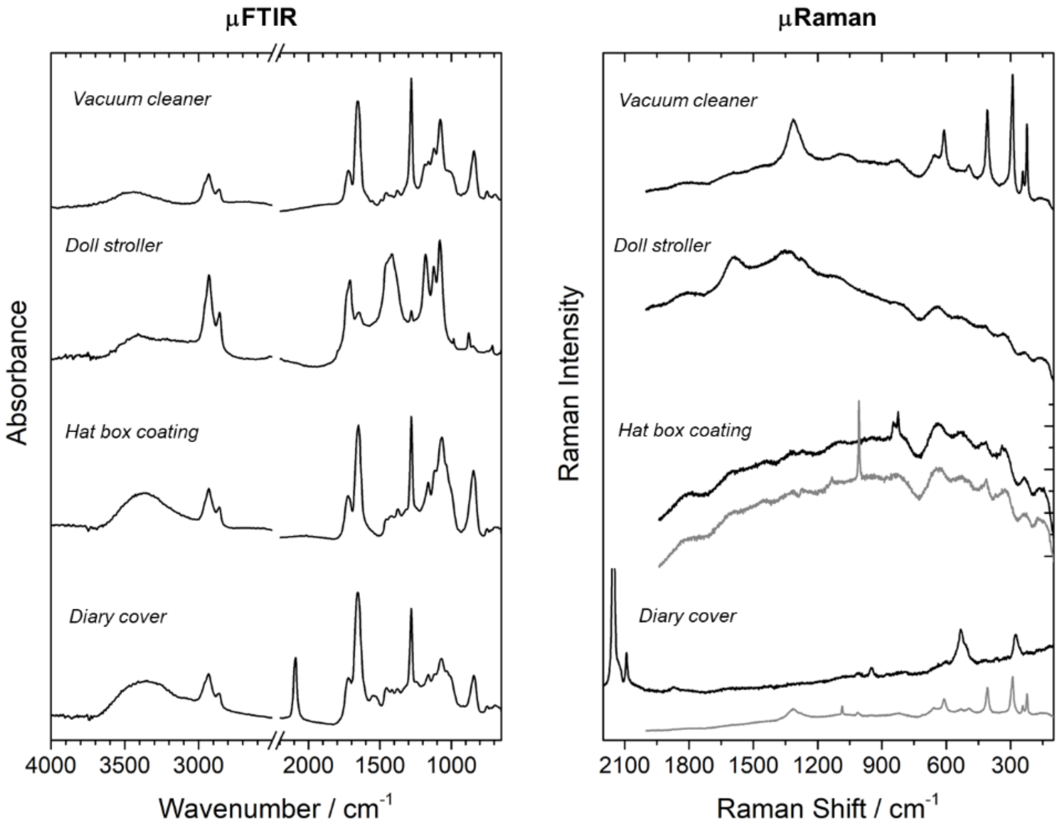


Figure 6. Analysis of the coatings collected from the National Museum of Costumes: *a)* Infrared and *b)* Raman (633 nm laser, 0.17 mW, 30-120s acquisition time, 1-5 cycles) spectra. For the diary cover, an extended spectral window (2200-100 cm^{-1}) was used to observe the $C\equiv N$ vibrations of Prussian blue.

Table 3. The "nappas" from the National Museum of Costumes: description of the objects, µInfrared and µRaman characterization.

Object	Description	µFTIR / cm^{-1}	µRaman / cm^{-1}
	Vacuum cleaner; Metal covered with a dark red "nappa". Brand: "Electrolux" (1940s)	Cellulose nitrate: 1652, 1280, 841, 750 Oil: 2930, 2860, 1461, 727	Iron (III) oxide: 1313, 609, 494, 409, 290, 223
	Doll Stroller made of wood. Opening and closing hood, made of green "nappa", supported by a metal structure (1930s)	Cellulose nitrate: 1647, 1280, 847, 750 Oil: 2924, 2853, 1461, 723 Barium Sulfate: 1180, 1123, 1080, 983 Calcium Carbonate: 2520, 1427, 877, 713	Carbon Black: 1587, 1349 Overall, intense fluorescence background
	Hat box covered with brown "nappa" (1920s-1950s)	Cellulose nitrate: 1650, 1280, 845 Oil: 2930, 2860, 1454	Chrome Orange: 846, 824, 339 Calcium Sulfate: 1134, 1007, 413
	Diary with a cover made of dark blue "nappa", with gold painted stripes on the spine (1960s-1970s)	Cellulose nitrate: 1654, 1280, 841, 750 Oil: 2932, 2860, 1461 Prussian Blue: 2091	Prussian Blue: 2153, 2090, 1005, 948, 572, 275 Iron (III) oxide: 1315, 610, 494, 407, 290, 223 Calcium Carbonate: 1086

Conclusions

This study calls for increased attention from museums and the conservation community towards cellulose nitrate-coated fabrics. We show evidence that these materials were widely used across various object typologies until the 1960s.

The microscale heterogeneous nature of cellulose nitrate heritage presents significant conservation challenges. The celluloid detachable collars examined are in good conservation condition, featuring fabric coatings composed of cellulose nitrate, camphor, anatase (TiO_2), and a carbon-based material. Conversely, systems combining cellulose nitrate with castor oil are particularly problematic. The significant technical insight provided by the Du Pont 1922 report on Fabrikoid degradation aligns with our analysis, indicating that oil oxidation results in the formation of free fatty acids and zinc carboxylates, such as zinc palmitate and stearate. Zinc oxide (ZnO) was absent in the Fabrikoid sheets and detachable collars, suggesting that DuPont replaced zinc oxide with anatase (TiO_2). The exact zinc source contributing to zinc soap formation remains unclear, but our findings suggest the use of lithopone ($BaSO_4$ + ZnS), leading to zinc sulfide (ZnS) consumption through saponification. Despite DuPont's recognition of lithopone's detrimental effects, its continued use prompts inquiry. Fatty acid compatibility with cellulose nitrate should be investigated due to the structural differences of ricinoleic acid compared to palmitic and stearic acids. Additionally, the role of anatase as a photodegradation catalyst prompts further exploration into whether carbon-based materials can mitigate potential adverse effects. Further study on the reactivity of colorants, such as Prussian blue and chrome yellow, in cellulose nitrate-castor oil systems is also needed. The Fabrikoid set examined represents one of many significant samples stored at the Hagley Museum and Library. This study shows how these resources, combined with technical data from DuPont, can provide invaluable insights into the chemical stability of early imitation leathers. Systematic characterization of all Fabrikoid samples, production of references based on industrial formulations, and artificial aging studies are crucial next steps toward comprehensively understanding the degradation mechanisms of these materials and developing effective conservation strategies. Involving experts in oil painting degradation will add essential knowledge to the reactivity of fatty acids in historical materials. The information obtained from these studies will be relevant to historians of plastics, particularly in discussions about the stability of Hyatt's celluloid compared to Parkes's Parkesine or Daniel Spill's xylonite formulations.

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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.

KEYWORDS
White deposits
Cleaning
Adipic acid
Thermoplastic polyurethane
Coatings
Fashion and design

Resumo

Os tecidos revestidos com poliuretano termoplástico (TPU) são comumente encontrados em coleções de moda e design em napas 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 espetroscopia de infravermelho. Os melhores resultados foram obtidos com agar-agar, tendo sido reconhecidas algumas limitações.

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].

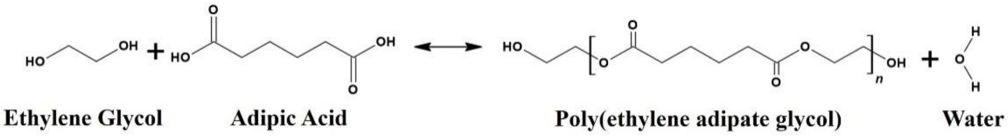


Figure 1. Examples of blooming visual appearance in TPU coated fabrics from fashion case studies produced: *a)* 1960s; *b)* 1970s; *c)* 1980s; *d)* 1990s; *e)* 2000s.

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.

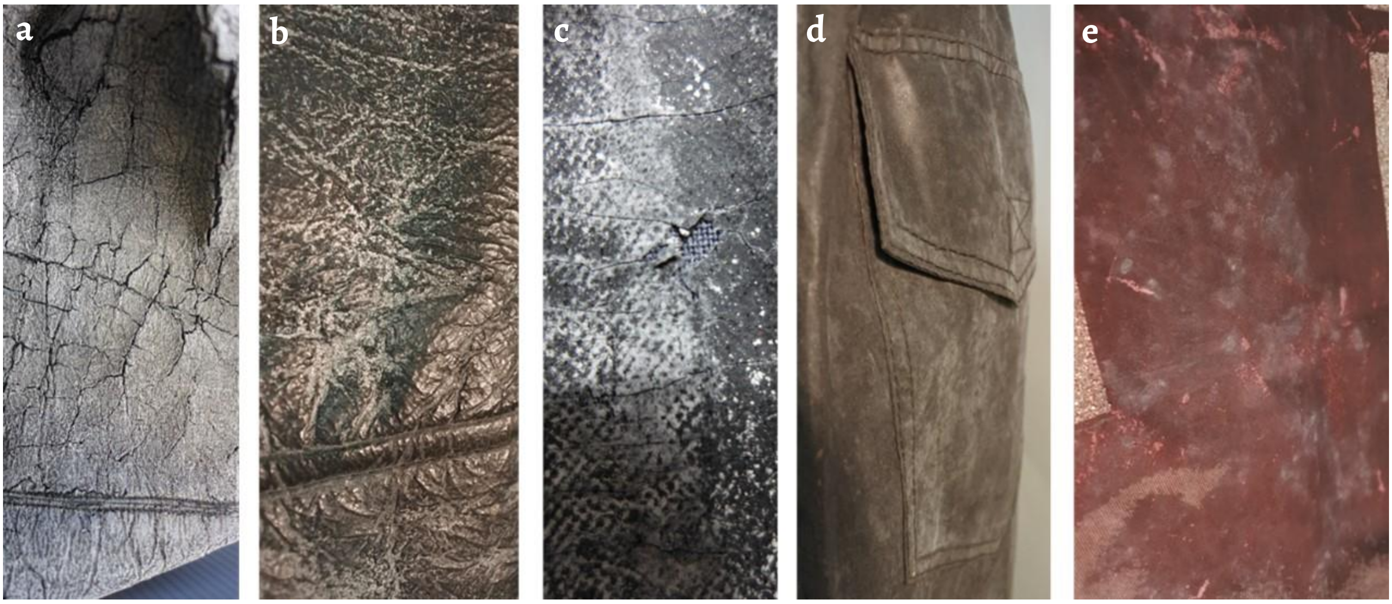


Figure 2. Examples of blooming visual appearance in TPU coated fabrics from fashion case studies produced: *a)* 1960s; *b)* 1970s; *c)* 1980s; *d)* 1990s; *e)* 2000s.

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.

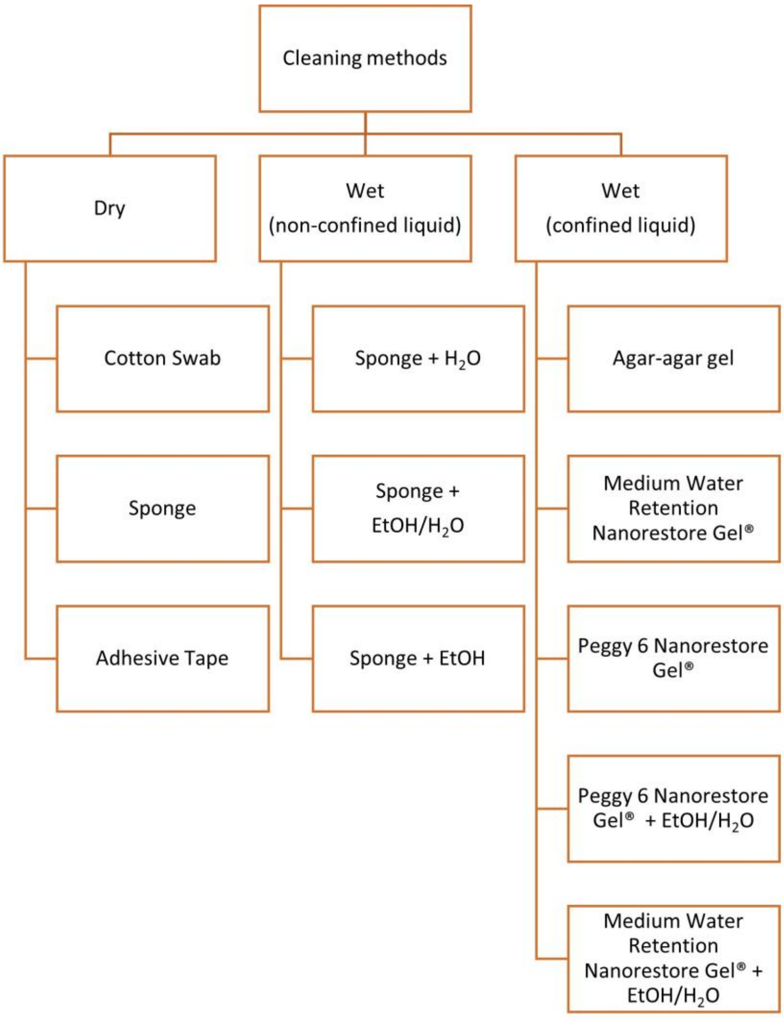


Figure 3. Scheme of the cleaning methods tested in the current study for the removal of blooming from ester-based aromatic TPU-coated fabrics.

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 ~10×).

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° 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 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 cm^{-1} were acquired with a diamond ATR module, 128 scans and 4 cm^{-1} resolution. Background spectra (air) were collected between every acquisition.

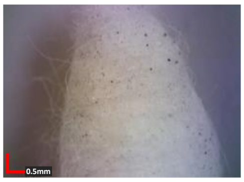
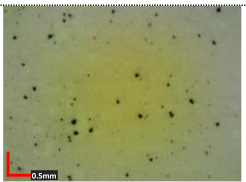
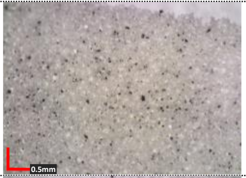
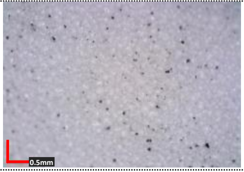
As adipic acid is formed through hydrolytic attack, it was important to assess if aqueous cleaning would imply an increase in the water content of the fabrics, possibly promoting blooming in the future. Since no equipment capable of directly measuring the water content of synthetic-coated fabrics was 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.

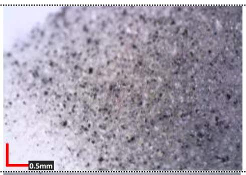
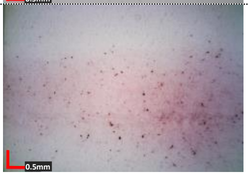
Results and discussion

Assessing cleaning strategies

Delta L* (ΔL*) 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 (ΔL*) 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 ΔL* 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* (Δ*L**) coordinate values and image of the cleaning tool/vehicle after blooming removal.

Sample	Cleaning method		ΔL*	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_2O	-5.89	
		Sponge + H_2O/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_2O/EtOH (50/50 %)	-3.17	
		MWR + H_2O/EtOH (50/50 %)	-3.03	
More deteriorated TPU-coated fabric (black and red jacket)	Wet | Non-confined liquid	Sponge + H_2O	-6.13	
	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 (ΔL*=-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 ΔL* was verified.

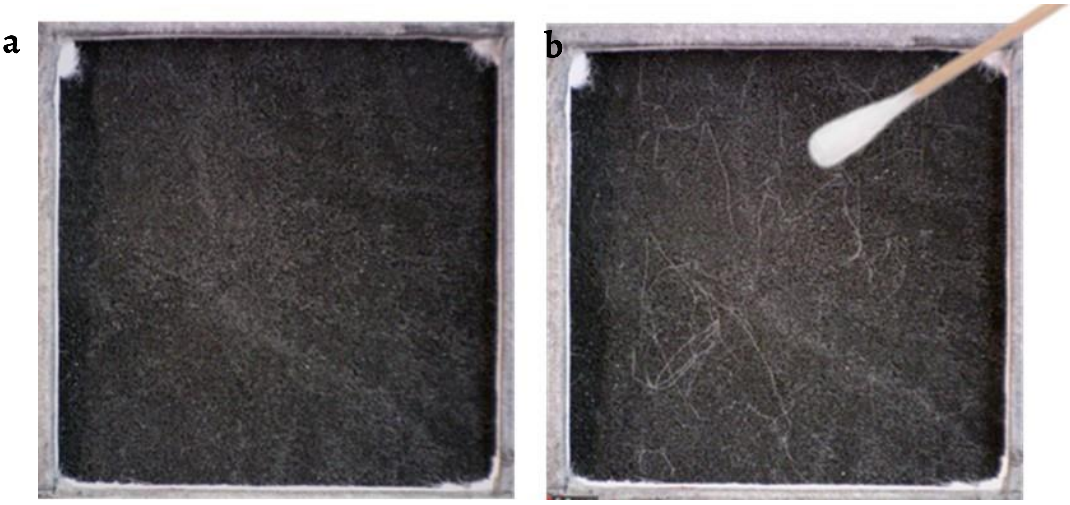


Figure 5. Less deteriorated TPU-coated fabric with blooming: *a)* before and *b)* after dry-cleaning with a cotton swab.

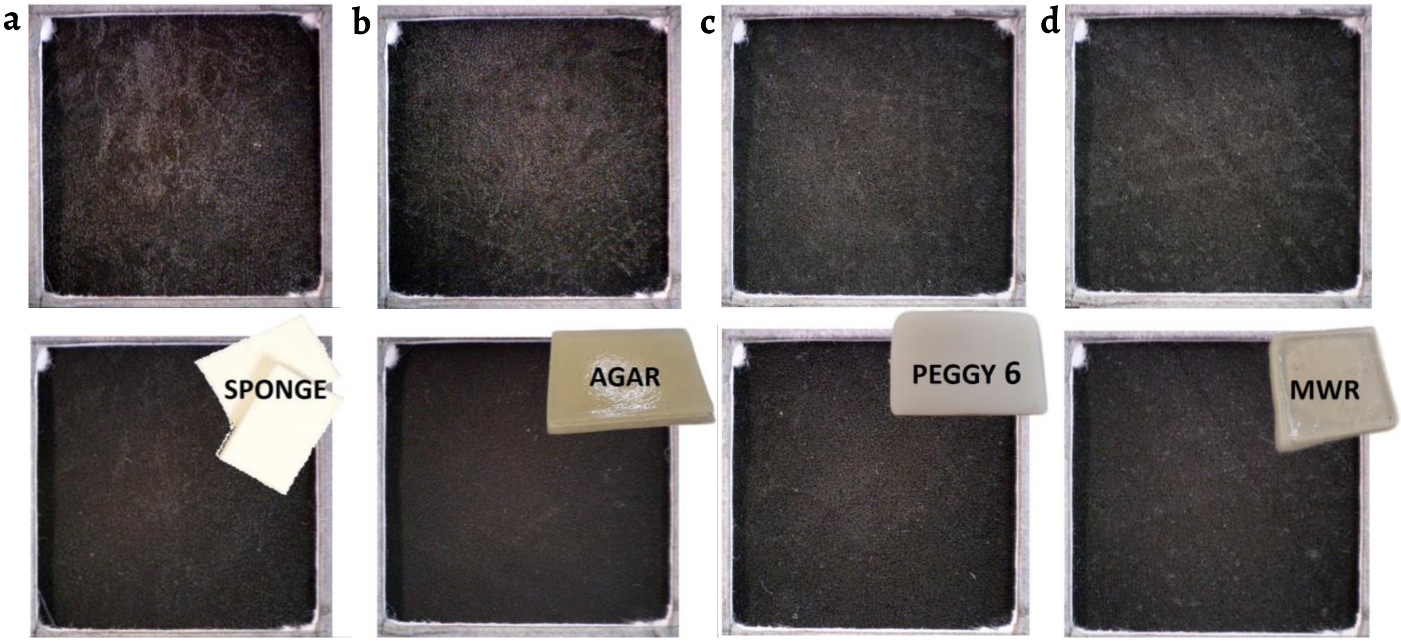


Figure 6. Less deteriorated TPU-coated fabric with blooming, before (top) and after (bottom) wet cleaning methods: *a)* sponge with water; *b)* agar-agar; *c)* Peggy 6; *d)* MWR.

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 cm^{-1} and bands at c. 1689, 1276 and 1192 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.

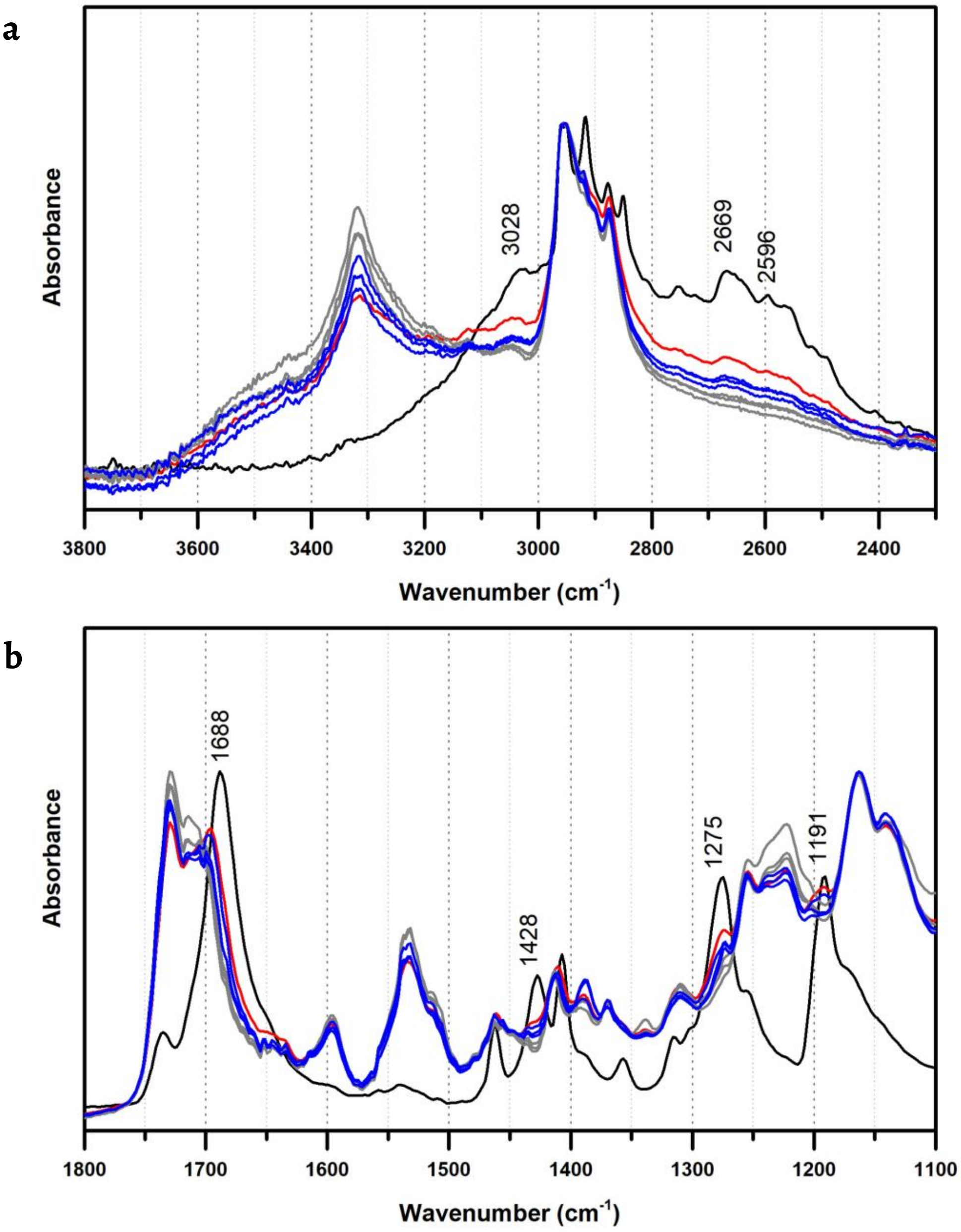


Figure 8. Infrared spectra (ATR-FTIR) of the highly fragile TPU-coated fabric featuring blooming after cleaning with sponge/water (blue) and agar-agar gel (grey): *a)* between 3800 and 2300cm^{-1}; *b)* 1800 and 1100 cm^{-1}. Black line corresponds to adipic acid spectrum and red line to a representative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

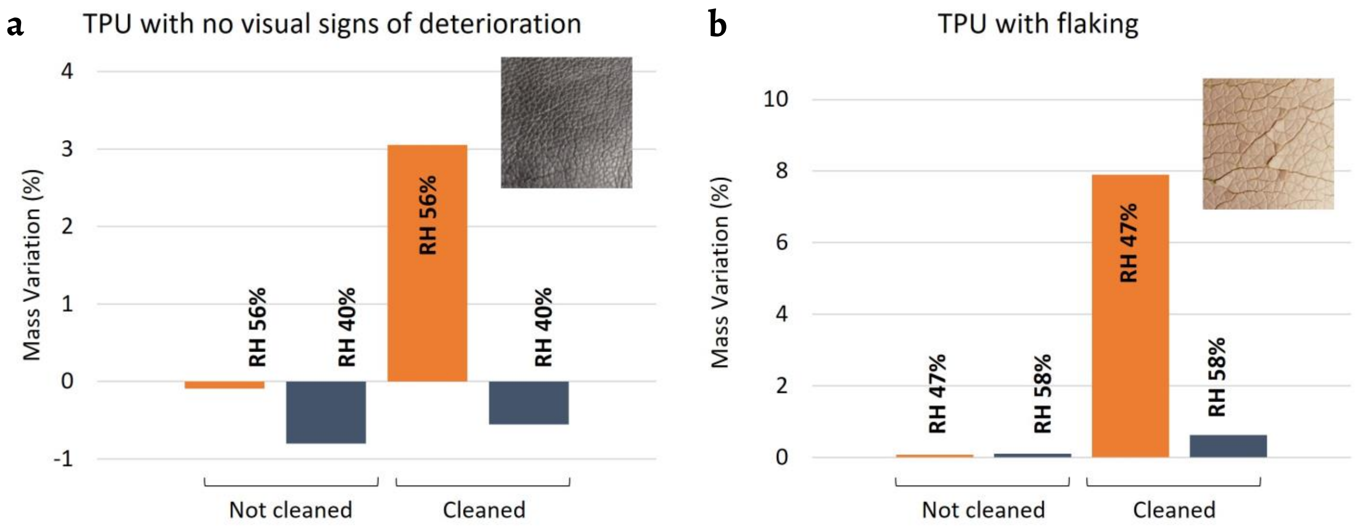


Figure 9. Mass variation (%) measurements of TPU-coated samples (cleaned and not cleaned) after 1 h (orange bars) and 1 day (grey bars): *a)* TPU with no signs of deterioration; *b)* TPU with flaking Inset: images of the TPU-coated samples submitted to this assessment.

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.

Acknowledgements

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Beyond the surface: a closer look at the stratigraphy of synthetic-coated fabrics in fashion collections and commercial samples through optical microscopy

Para além da superfície: um estudo sobre a estratigrafia de tecidos com revestimentos sintéticos em coleções de moda e amostras comerciais através de microscopia ótica

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Abstract

Synthetic-coated fabrics, often made of short-life expectancy coatings, namely plasticised poly(vinyl chloride) (p-PVC) and thermoplastic polyurethane (TPU), are challenging to preserve. These materials are poorly studied within the conservation field, and there is a lack of research and solutions for their preservation. This study aimed to provide insight into the yet unknown variability of p-PVC and TPU-coated fabrics in fashion collections. The subtle differences in layer construction and morphology were investigated in a selected set of materials to unveil production methods and better understand delamination damages, namely peeling and flaking. Optical microscopy provided primary material assessment, complemented by ATR-FTIR for molecular identification. A wide variability of synthetic-coated fabrics was reported and connections between morphology, production methods and delamination damages were suggested. Optical microscopy proved to be a powerful tool in the study of the stratigraphy of coated fabrics, enhancing material knowledge for more informed conservation decisions.

KEYWORDS
Thermoplastic polyurethane
Poly(vinyl chloride)
Coatings
Cross-section
Synthetic textiles
Heritage conservation

Resumo

Os tecidos revestidos, frequentemente compostos por revestimentos efémeros, como o poli(cloreto de vinilo) plastificado (p-PVC) e o poliuretano termoplástico (TPU), são materiais de difícil preservação. Estes materiais são ainda pouco estudados na área da conservação, existindo uma lacuna de investigação e soluções para a sua preservação. Este estudo visa demonstrar a variabilidade dos tecidos revestidos com p-PVC e TPU em coleções de moda. As diferenças subtis na construção e morfologia das camadas de um conjunto de materiais foram investigadas, para desvendar métodos de produção e melhor compreender danos causados por destacamento, nomeadamente *peeling* e *flaking*. Os materiais foram analisados por microscopia ótica, complementada por ATR-FTIR para identificação molecular. A ampla variabilidade destes tecidos é apresentada e sugerem-se relações entre morfologia, métodos de produção e danos por destacamento. A microscopia ótica provou ser uma ferramenta vantajosa neste estudo, permitido um avanço no conhecimento para decisões de conservação mais informadas.

PALAVRAS-CHAVE
Poliuretano termoplástico
Poli(cloreto de vinilo)
Revestimentos
Corte estratigráfico
Tecidos sintéticos
Conservação do património

Introduction

A coated fabric is characterised as a multilayer construction composed of two or more layers, in which at least one should be a textile fabric and another a substantially continuous polymeric layer. The bonding of these layers occurs by means of their own adhesive properties or by an additional adhesive layer [1]. The application of a coating layer to a textile fabric significantly influences the external characteristics and physical properties of the final product [2] by granting a new aesthetic, such as a highly glossy or leather-like appearance, or additional technical or functional properties, including flame retardancy or fire-resistance, waterproofness, and improved solvent and abrasion resistance [2-3].

Fabrics have been coated for several centuries with the natural materials available, such as linseed oil, wax emulsions, and natural rubber [3-6]. More recently, in the nineteenth and twentieth centuries, advances in chemistry and textile technology allowed the development of new semi-synthetic and synthetic polymer materials, several of which came to be used as fabric coatings, and new processing coating techniques [3-4, 7]. Synthetic-coated fabrics paved their way into several industries and fields due to their broad range of physical and chemical properties and the ability to be tailored-made to meet specific requirements, including casual and sports apparel, protective clothing, household textiles and transports [2-4].

Many items made of synthetic-coated fabrics have become collectable pieces, and their presence in modern museum collections worldwide has significantly increased as a reflection of their widespread application in several fields, technological development, and artistic and societal preferences over time. Examples include garments, shoes and accessories in costumes and fashion [8-13], upholstery furniture in product design [14-16] and even spacesuits in astronautics [17]. However, the conservation of synthetic-coated fabrics presents a significant challenge due to the lack of awareness of their presence in museum collections, possibly related to the many visual looks that these fabrics can assume, and the lack of studies in the field; diverse production methods that result in complex and composite materials, many times combining natural and synthetic materials; and a large variety of ageing behaviours. In addition, these materials often have a shorter life expectancy compared to traditional fabrics and textiles, making their preservation particularly difficult [7-8, 11, 18]. All these factors pose challenges to identifying and recognising synthetic-coated fabrics as priority materials in museum collections preservation.

Synthetic-coated fabrics can be composed of several layers of different materials. As coatings, several semi-synthetic and synthetic polymers have been applied to fabrics, including cellulose nitrate (CN), cellulose acetate (CA), synthetic rubbers, acrylics, poly(vinyl acetate), plasticised poly(vinyl chloride) (p-PVC) and thermoplastic polyurethane (TPU) [3-4]. Many of these materials, such as CN, CA, p-PVC and TPU, are already known by the conservation community for their unstable and ephemeral nature, which leads to early signs of deterioration and premature loss of iconic objects [7, 18-19]. In addition, and further contributing to the complexity of these materials, additives can be incorporated into their formulation to confer specific properties, including plasticisers, anti-ageing additives (light and heat stabilisers, antioxidants), fillers and colouring agents, which can significantly influence the deterioration of the material [7, 20]. Regarding the fabric substrate, a wide range of natural and synthetic fabrics can also be used, including cotton, polyester and polyamide, in knitted, woven and non-woven constructions [2-4].

Numerous application techniques have been developed throughout the last decades to produce coated fabrics, which can be categorised on a different basis, such as equipment used or the form of the coating material [3]. Concerning how a coating is applied to a fabric substrate, two important techniques can be distinguished: the direct and the indirect coating methods. The direct coating is the oldest method and is still applied today. It consists, as the name indicates, of the direct application and homogeneous spreading of a coating compound onto a fabric, which can be achieved by means of different techniques such as spraying, knife coating or a roller system [2-4]. This method is usually not suitable for open-structure fabrics, such as knitted ones, as penetration of the coating compound into the fabric might occur, or for stretchy fabrics, as they need to be pulled flat for proper coating application [3-4]. Alternatively, these fabrics can be coated by the indirect method, also known as transfer coating. Instead of applying the coating directly onto a fabric, it is first applied onto a release paper, which acts as a temporary support, and spread using the same techniques as in the direct method. Coating and release paper are then laminated to a fabric substrate either by the adhesive properties of the coating itself or by adding an adhesive layer (tie-coat) before introducing the fabric. The final step is the removal of the release paper [2-4]. Resin penetration into the fabric is low or non-existent with this method since the coating is usually in a film form when it comes into contact with the substrate [2, 4].

The transfer coating method was an important development in the coated fabrics industry, especially for producing imitations of leather, as it offered several advantages over the direct method. It has been applied to fabrics at least since the 1940s [21], followed by continuous advancements that shaped the machinery and materials used [22-27]. This method was first developed to overcome a particular limitation of CN as a coating - its low viscosity, which at the time could only be applied to tightly woven and thus more expensive fabrics to avoid excessive penetration [28]. The transfer method allowed for a more versatile and less expensive coating process, enabling the application of thinner coating layers to virtually any fabric of choice, even the simpler, low-cost and open-structure ones. As it minimised coating penetration, it allowed the production of fabrics with improved hand and suppleness [2, 4, 28-29]. Additionally, transfer coating facilitated embossing using customised patterned released paper, ideal for simulating leather texture [2, 28]. While CN, CA, and PVC were mentioned in early transfer-coating patents in the 1940s [21-27], not all synthetic compounds were readily compatible with the method once introduced to the market. Polyurethanes, for example, started to be applied to fabrics in the 1950s by the direct method as a two-component system [29-30], although their application by the transfer method was only possible in the 1960s with the development of the one-component system [30-32]. This formulation offered greater stability, longevity, and ease of application, resulting in high-quality, durable, and resistant coatings [29-32].

Despite the challenge synthetic-coated fabrics represent, these materials are still poorly studied within the conservation field, and adequate conservation strategies for their preservation are still lacking. The first research steps into this subject were taken by the Glossy Surfaces research project (2020-2023), an international consortium of museums (MoMu, Belgium; MUDE, Portugal; MET, USA) and research centres (DCR LAQV-REQUIMTE, Portugal; Centexbel, Belgium), entirely focused on the study and preservation of synthetic-coated fabrics in fashion collections from the 1960s until now. Within this timeframe and collection type, there are few existing studies researching these materials, most of which have resulted from the Glossy Surfaces project. These studies have mainly focused on identifying the chemical composition and damages of the synthetic-coated fabrics. TPU and p-PVC were found to be the most prevalent coating materials [8, 33], especially ester-based and aromatic TPUs [8-10]. These polymeric materials have been on the market as coatings ever since the mid-twentieth century [5, 34], due to their highly appreciated physical properties and for being particularly excellent options for rainwear and imitations of leather, namely TPUs [2]. Cotton, polyester, polyamide and leather were the most commonly found fabric substrates, the latter predominately identified within the domain of footwear and accessories [10]. Regarding damages of the synthetic coatings, several have been identified and reported, the most common patterns being blooming (mostly caused by adipic acid [9-10]), stickiness, peeling, flaking and cracking [8, 35]. França de Sá et al. also identified blooming as being the main damage for ester-based aromatic TPUs, while ester-based aliphatic coatings were more prone to stickiness when deteriorated [10]. Nevertheless, no studies were found within the conservation field that explored the variability of these materials based on manufacturing processes and their possible influence on the observed damages.

The present study started during the Glossy Surfaces project. It aims to fill this knowledge gap by providing new insight into the variability of p-PVC and TPU-coated fabrics in the context of fashion collections, the two most found coating compositions during the project. Although the Glossy Surfaces project covered the period from the 1960s until now, the present study focused on the timeframe from the 1970s until the present decade. Production methods were unveiled based on the analysis of the layer construction and morphology of the coated fabrics, and their possible impact on damages was explored, namely flacking and peeling. This study focused on the visual analysis of the cross-sections through optical microscopy (OM) as the main source of information, aiming at developing a first-step characterisation methodology that could be easily implemented by most museums and cultural institutions holding these materials in their collections. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was used as a complementing tool. This research is a step forward in advancing the knowledge of synthetic-coated fabrics within fashion collections and in developing suitable conservation strategies.

Materials and methods

Sample selection

During the Glossy Surfaces project, a representative set of more than 100 synthetic-coated fabric samples from fashion museum collections worldwide was collected for analysis. It included clothing, shoes, and accessories covering the period from the 1960s until now, different stages of deterioration, and the most common damage patterns. Most of these samples did not show a complete stratigraphy of the coated fabrics since collecting full cross-sections from fashion museum items poses particular difficulties, especially from footwear, due to the lack or even inexistence of hidden areas to collect samples unnoticed and without damaging the integrity of the item.

From the Glossy Surfaces set of samples, a minor set showed a complete cross-section, which was crucial for the present study, and was further analysed. In addition, several case study fabrics and items, donated or acquired and with no cultural value, were included in the research, from which it was possible to collect the complete stratigraphy without worrying about potential damages. Custom-made coated fabrics produced by Centexbel (Ghent, Belgium) were also included in the study for comparison. These samples were composed of ester-based TPU coatings, both aliphatic (Impranil DSL/1, Covestro AG, Leverkusen, Germany) and aromatic (Laripur S860, COIM, Milan, Italy), with no additive added to the formulation. Both TPU coatings were directly applied to polyester and cotton fabrics and transfer-coated to a leather substrate.

In total, the set analysed in the present study comprised c. 70 samples, composed of TPU and p-PVC-coated fabrics from the 1970s until now. It was not possible to include complete cross-section samples of items from the 1960s in this research. The set analysed included unaged and aged materials showing the most common damage patterns (blooming, stickiness, flaking, and peeling) in different stages of deterioration (slightly deteriorated, deteriorated and severely deteriorated).

Sample characterisation

Empirical assessment

A first evaluation of the properties of the selected samples was conducted under low magnification using a stereomicroscope. The samples were observed and manipulated for an initial assessment of the different layers regarding number, thickness, colour, pliability, and overall appearance. The level of attachment of the layers was also evaluated, in particular to determine the possible presence of an adhesive layer.

Samples from fashion museum items were only slightly manipulated to avoid destruction and the need to collect more samples for future analysis. However, samples from the acquired or donated case study fabrics and items were manipulated and deconstructed with the help of tweezers and scalpers for a better understanding of the properties of the different layers. This destructive analysis was possible due to a larger amount of material available for sampling and the absence of historical value.

Optical microscopy imaging

The top surface and cross-section of all samples were observed under reflected (incident) light in brightfield, darkfield, cross-polarized and fluorescence modes. The method for sample preparation for analysis and to acquire cross-section images is described elsewhere [10].

The images presented are representative of the coated fabrics analysed, which, as previously described, included samples from museum items and non-cultural materials. Due to the limited size of museum samples, it was more difficult to obtain clear cross-section images. Thus, most of the images presented are from representative non-cultural materials, allowing for better visualization of the stratigraphy since there were no size limitations for sample collection. Table 1 provides a detailed description of the sample cross-sections presented in this study.

Micrographs were acquired using an Axioplan 2ie Imaging system (Zeiss, Germany) equipped with an incident halogen (tungsten-halogen light source, HAL 100) and UV radiation (mercury light source, HBO 100) illuminators and coupled with a DXM1200F digital camera and ACT-1 control software (Nikon, Japan). The samples were analysed using ocular lenses with a magnification of 10x and Epiplan objective lenses with magnifications of 5× and 10× for a total optical magnification of 50× and 100×, respectively. The scales for all objectives were calibrated within the Nikon ACT-1 control software. Fluorescence microscopy images were acquired with blue-violet light (Zeiss Filter set 05 – excitation BP 395-440 nm, beamsplitter FT 460 nm, emission LP 470 nm) and ultraviolet light (Zeiss Filter set 02 - excitation G 365 nm, beamsplitter FT 395 nm, emission LP 420 nm).

Table 1. Description of the origin of the sample cross-sections presented in this study.

Table/Figure		**Origin**
Table 2	a)	Runaway jacket (2000) from the Museu do Design e da Moda – MUDE
	b)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	c)	Sample donated by Rossimoda (Venice, Italy)
	d)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	e)	Ready-to-wear purse (2000) from the Palais Galliera – Musée de la Mode de la Ville de Paris
Figure 1	a)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	b)	Ready-to-wear shorts (1996) from the ModeMuseum – MoMu
Figure 2	a)	Ready-to-wear dress (1970) from the Museu do Design e da Moda – MUDE
	b)	Ready-to-wear jacket (c. 2020) donated to the Glossy Surfaces project, naturally aged and damaged by flaking
Figure 3	a)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	b)	Ready-to-wear jacket (1990s) from the André Courrèges Archive
	c)	Ready-to-wear parka bought at a second-hand store (Brussels, Belgium) in 2022, naturally aged and damaged by stickiness
Figure 4	a)	Ready-to-wear jacket donated to the Glossy Surfaces project (2010), naturally aged
	b)	Commercial fabric bought in 2023 (Lisbon, Portugal)
Figure 5	a)	Commercial fabric bought in 2023 (Lisbon, Portugal)
	b)	Commercial fabric bought in 2022 (Lisbon, Portugal)
Figure 6	a)	Commercial fabric bought in 2022 (Lisbon, Portugal)
	b)	Ready-to-wear jacket (c. 2010s) donated to the Glossy Surfaces project, naturally aged and damaged by peeling
Figure 7	a)	Ready-to-wear jacket (c. 1990s), donated to the ModeMuseum – MoMu
	b)	Ready-to-wear jacket (unknown date), donated to the ModeMuseum – MoMu
Figure 8	a)	Ready-to-wear jacket (c. 2020) donated to the Glossy Surfaces project, naturally aged and damaged by flaking
	b)	Ready-to-wear jacket (c. 2010s) donated to the Glossy Surfaces project, naturally aged and damaged by flaking
	c)	Fabric (c. 2010s) donated to the Glossy Surfaces project, naturally aged and damaged by flaking

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflection Fourier transform infrared spectroscopy (ATR FTIR) was used to determine the chemical composition of the top coating, substrate and, whenever present and possible to analyse, the intermediate layer(s) of the samples. In the present study, ATR-FTIR was only used as a complementing tool for a more informed establishment of connections between material composition and visual characteristics observed under the OM regarding the layer construction, morphology and damages.

ATR-FTIR was carried out with the Handheld Agilent 4300 spectrophotometer (Agilent, USA), equipped with a ZnSe beam splitter, a Michelson interferometer and a thermoelectrically cooled DTGS detector. Spectra were acquired with a diamond ATR interface, 128 scans and a resolution of 4 cm^{-1} in the spectral region between 4000 and 650 cm^{-1}. This ATR interface allows the analysis of samples with a minimum size of 200 microns. Background spectra were collected between every acquisition. Spectral analysis was performed using Omnic32 and OriginPro 8 software.

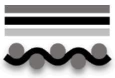
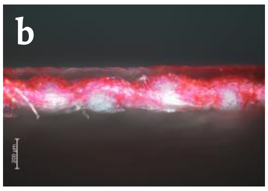
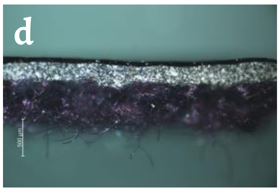
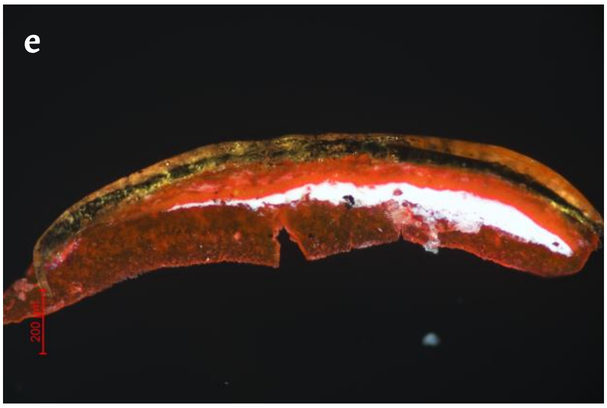
Results and discussion

Layer construction: visible and hidden layers

As expected, the analysed set of coated fabric cross-sections showed a variable number of layers under visible light (Table 2). The most common stratigraphy were two-layer constructions, solely composed of a top polymeric coating on a fabric substrate (examples a and b), or three-layer, which also included an additional intermediate coating layer between these two (examples c and d). Coated fabrics with more complex layer build-ups composed of four or more layers, as shown in Table 2 (example e), were less commonly found.

The thickness of the analysed samples also varied, even between coated fabrics with similar layering construction, i.e., the same number of layers. It varied from very thin (less than 1 mm), such as lightweight raincoats (Table 2, example b), to thicker, like some imitations of leather (example d) or coated leathers (example c), the latter more often found in footwear and accessories. The relationship between thickness and the number of layers is not a straightforward one. It is a complex interplay that is influenced by the desired aesthetic, suppleness, and function of the final product. Additionally, the production method employed might also play a role, as will be delved into in more detail in the following chapter.

Table 2. Microscopy images of cross-section examples of synthetic-coated fabrics (see Table 1) under cross-polarized visible light, showing a varied number of layers: two (a and b); three (c and d) and more than four (e).

Cross-sections			
Number of layers	2	3	≥ 4
Scheme			
Examples	 	 	

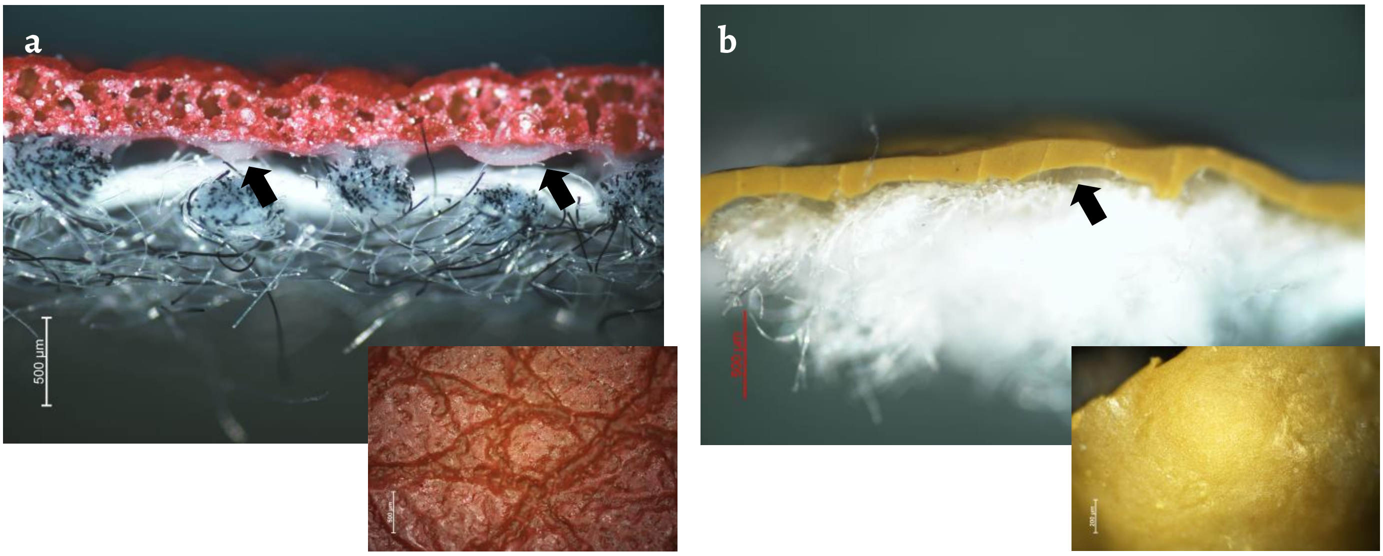


Figure 1. Microscopy images of: *a-b)* two cross-section examples of synthetic coated fabrics (see Table 1) under cross-polarised visible light composed of three layers, in which the intermediate one (arrows) was possibly added for adhesive purposes. Insets: top views of the respective coated fabric.

As observed in Table 2, each layer might play a different role in the final aesthetic and properties of a coated fabric. The colour might be introduced either by the top coating layer (examples a and d), an intermediate layer if present (example c), or even by the fabric substrate (example b). On the other hand, when a glossy finish is desired, it is, in most cases, obtained by an uncoloured top layer, as observed in Table 2 (examples b, c and e).

In addition, intermediate layers might be added for adhesive purposes, i.e., to promote the bond between the coating layer(s) and the fabric substrate [4]. Examples of such layers visible under visible light are shown in Figure 1 (highlighted by black arrows).

The presence of this layer indicates that the coated fabrics might have been produced by the transfer coating method, as will be discussed in more detail in "Coating morphology" section. As observed in these images, the level of contact of this type of layer with the substrate varies, as the adhesive might be more (Figure 1b) or less (Figure 1a) impregnated within the fibres of the substrate. In the latter, the observed voids between the two layers might be seen as weak points in the fabric structure, which can lead to future damage at this interface, particularly delamination.

However, in most cases, adhesive layers are particularly difficult to detect under visible light for their transparency and thinness, and for frequently being impregnated within the fibres of the fabric substrate. To overcome this limitation, samples were also observed under blue-violet and ultraviolet radiation to detect fluorescence in case the layers had different fluorescence properties under these wavelengths (Figure 2). In some cases, as observed in Figure 2a, an additional layer was detected due to its distinctive fluorescence (right, highlighted by an arrow), while being barely visible under visible light (left). This sample was composed of a TPU coating and, while it was not possible to analyse the adhesive layer with the used techniques, it is likely composed of the same material for compatibility [32].

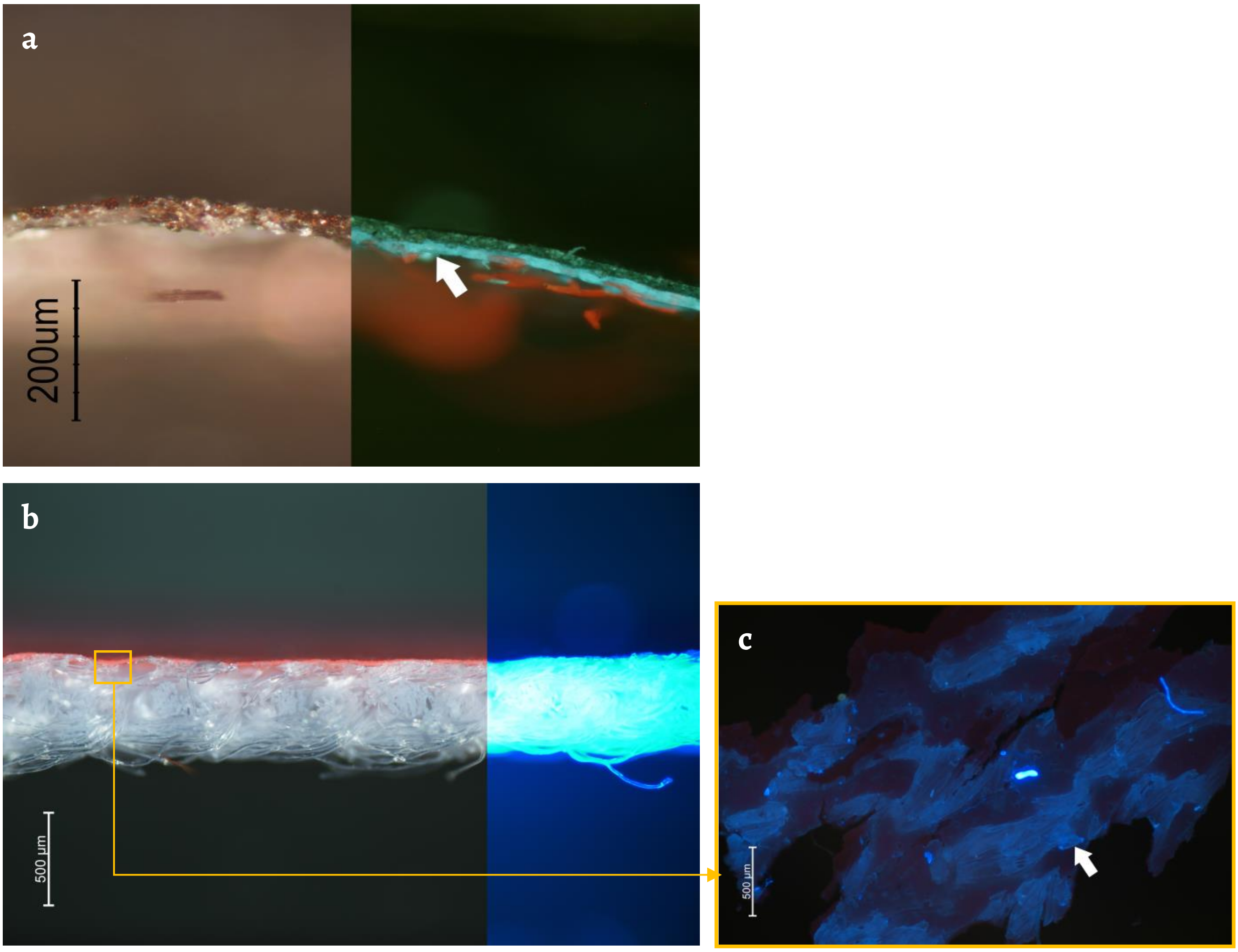


Figure 2. Microscopy images of two synthetic coated fabrics examples (see Table 1) composed of an intermediate layer, possibly added for adhesive purposes, only detectable under fluorescent illumination: *a)* cross-section of the dress sample under visible (left) and blue-violet (right) lights; and jacket sample: *b)* cross-section under visible (left) and ultraviolet (right) lights and *c)* bottom side of the top coating under ultraviolet light (arrows highlight the presence of the detected intermediate layer).

Unaged polyurethane is known for showing some fluorescence under both blue-violet and ultraviolet lights, corresponding to longer and shorter wavelengths, respectively, which can be attributed to the presence of aromatic structures and amide groups in its network, along with a predominance of non-oxidized forms [36]. However, previous studies have demonstrated that the fluorescence properties of several polymers, natural and synthetic, can suffer modifications due to ageing [37-41]. Particularly for polyurethane, observations with fluorescence microscopy showed that the fluorescence intensity of the material strongly increases with ageing, as a consequence of the formation of new fluorophores such as oxidised species and new conjugated bonds [36, 42]. However, the stronger fluorescence observed for the intermediate layer in Figure 2a compared to the top coating is believed to not be related to its more advanced deterioration state, but rather due to a more straightforward chemical formulation, possibly with fewer additives, such as pigments and fillers, since its function is to promote the bonding between the upper coating and substrate and not an aesthetic one. The presence of additives like pigments is also known to strongly influence the fluorescence properties of a material [43-45], which, in this case, might be masking the intrinsic fluorescence of the polymer.

This hypothesis is corroborated by the overall observations on the fluorescent properties of the analysed set of TPU-coated fabrics. Most of the analysed TPU top coatings showing colour did not particularly fluoresce under blue-violet or ultraviolet wavelengths, while the transparent TPU top coatings of most highly glossy coated samples strongly fluoresced under the same illumination conditions. Moreover, the reference coated-fabric samples custom-made by Centexbel composed of ester-based TPU coatings (both aliphatic and aromatic) with no additives incorporated into the formulation, also exhibited strong fluorescence. However, it is important to highlight that the same observations did not apply to coated fabrics composed of p-PVC coatings, as these did not show fluoresce properties under the same illumination.

Some of the analysed coated-fabric samples were composed of other layers that also showed a strong fluorescence, as the fabric substrate in Figure 2b, which disguised the presence of an additional intermediate layer. Several factors can influence the fluorescence properties of a fabric, including the chemical composition of the fibres, additives, treatments, and degradation [46]. If the destruction of the sample is possible, the substrate can be removed from the sample for further examination of the bottom side of the remaining coating layers(s), as shown in Figure 2c. In this case, clues of an additional layer were found, through the observation of traces of a heterogeneously spread material (white arrow) with a distinct fluorescence.

Coating morphology, chemical composition and processing techniques

As previously described, there are several manufacturing techniques to produce synthetic-coated fabrics. However, for the present research, the way a coating is applied to the fabric was considered of the most relevance, which is mainly done through the direct and transfer coating methods.

As previously mentioned, the direct method is not suitable for stretchy and open-structure fabric, like knitted ones, making it possible to discard this technique in the presence of such fabric substrates. The direct application and spreading of a coating on a fabric substrate leads to the formation of a compact continuous film that sinks into the weave of the fabric [3-4]. Figure 3a shows an example of a coated fabric produced by this method in which these characteristics can be easily observed.

On the other hand, the so-called transfer coating method can be used for the coating of knitted fabrics or others with open and stretchable constructions. The principle of this method can be summarised by the application and spreading of the polymer coating onto a release paper to form a continuous film, followed by the application of additional layers such as adhesive ones, lamination to the fabric substrate and removal of the release paper [2-4]. An example of a coated fabric produced by this method is shown in Figure 3b. Since the fabric substrate usually only comes into contact with the coating layer(s) after the latter is already in a film form, resin penetration tends to be low or even inexistent, as opposed to the direct method [2, 4]. In addition, the presence of an adhesive layer, also known as tie-coat, to promote the bond of the coating to the substrate is a good indicator that the coated fabric might have been produced by this method. Such a layer is not needed when a coating is directly applied since its sink-in into the fibres of the substrate is usually enough for good adhesion.

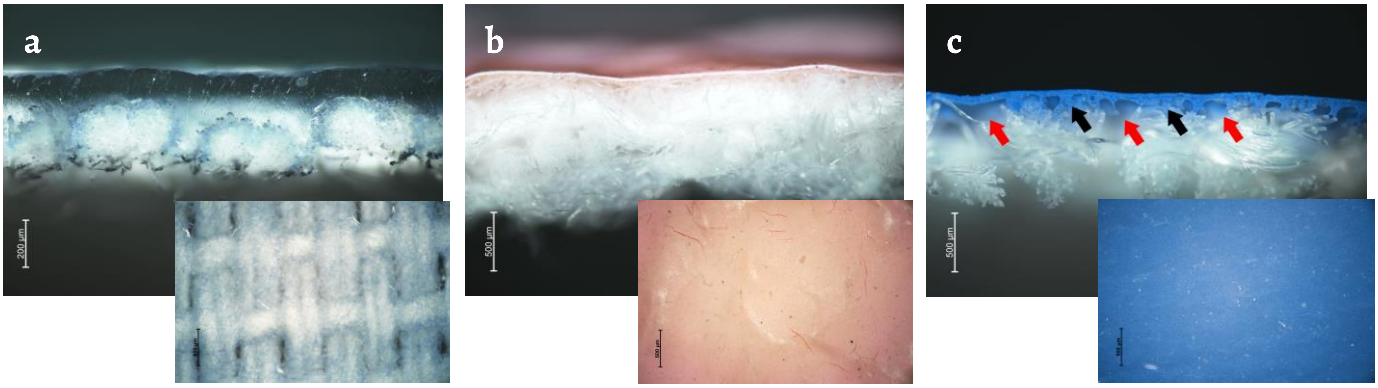


Figure 3. Microscopic images of cross-section examples of coated fabrics (see Table 1) under cross-polarised visible light possibly produced by: *a)* direct method; *b-c)* transfer coating method with complete and partial curing of the coating before lamination of the fabric substrate, respectively (red arrows indicate voids, while black arrows highlight contact areas between the coating and substrate). Insets: top views of the respective coated fabric.

However, coatings that are only partially penetrated within the weave of the fabric were also found, as the example shown in Figure 3c. At the interface between coating and substrate, voids can be observed (red arrows), i.e., areas of no contact between the layers, suggesting that the coating was possibly not applied by the direct coating method as it would have been fully impregnated within the fibres, as the example in Figure 3a. Instead, the coated fabric was more likely produced by the transfer coating method, although the coating was possibly only partially dried upon lamination of the fabric substrate, leading to the observed partial penetration of the coating into the fabric (black arrows), which does not usually occur with this method. The voids observed in this fabric can be pointed out as weak areas in its structure that might be more prone to future damage as, for example, humidity might be trapped in here, causing an imbalance between the layers and triggering the chemical deterioration of the coating [47].

Microporous coating structures were also detected within the analysed samples, obtained by different production techniques such as foamed and coagulation methods.

Examples of foam coatings are presented in Figure 4, in which the cells of the foams are clearly distinguished. These coatings usually have a leather-like appearance and tend to be bulkier than the compact continuous coatings, resulting in coated fabrics with an opaque look, and a soft and cushioned feel. Foam coatings are usually directly applied to the substrate although its penetration into the weave of the fabric does not occur. This method is thus suitable for woven and knitted fabrics, even the ones with relatively open constructions, that typically cannot be coated by the more conventional direct coating technique [4, 48]. Furthermore, the low penetration of the foam makes it possible to preserve the original properties of the fabric, like the soft drape [48]. These coating structures were found in both TPU and p-PVC-coated fabrics.

Other examples of microporous coating structures were detected, corresponding to coated fabrics with a soft and spongy feel, composed of porous TPU layers (Figure 5). These materials are distinguished from the foam coatings observed in Figure 4 by the reduced cell size. The observation of the samples under blue-violet and ultraviolet radiation provides finer image resolution than visible light due to shorter wavelengths [49], which proved useful in exposing more clearly the microporous structure of these samples (Figure 5b, right) for comparison with the literature [50-52].

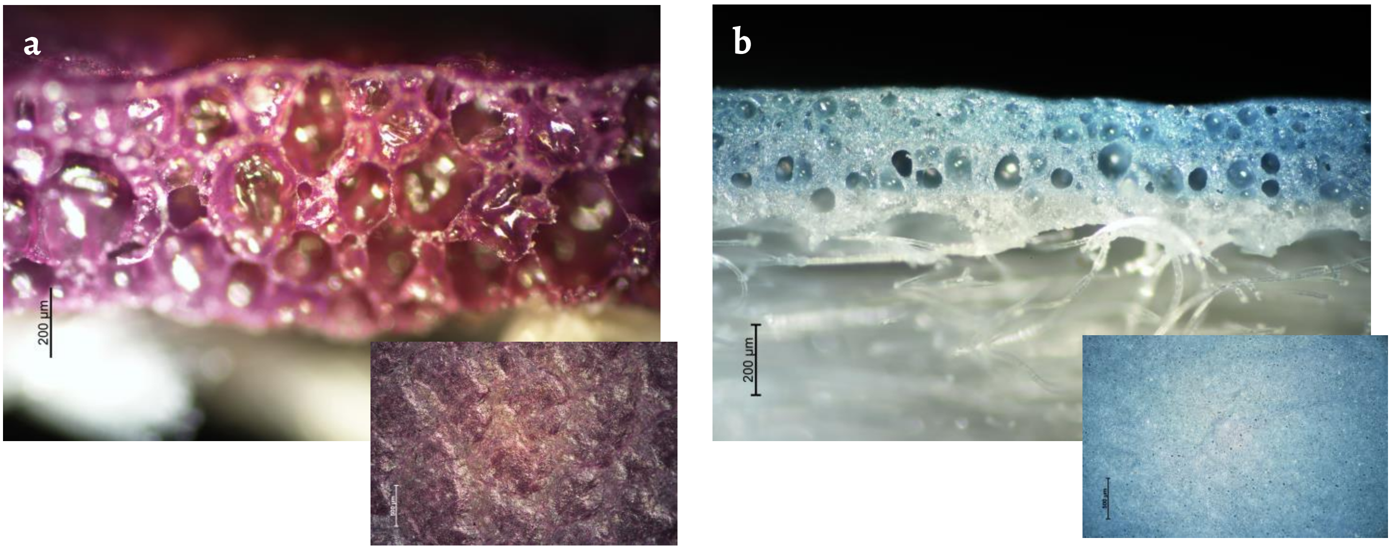


Figure 4. Microscopic images of two cross-section examples of coated fabrics (see Table 1): *a)* jacket and *b)* commercial fabric, under darkfield visible light composed of a foam coating. Insets: top views of the respective coated fabric.

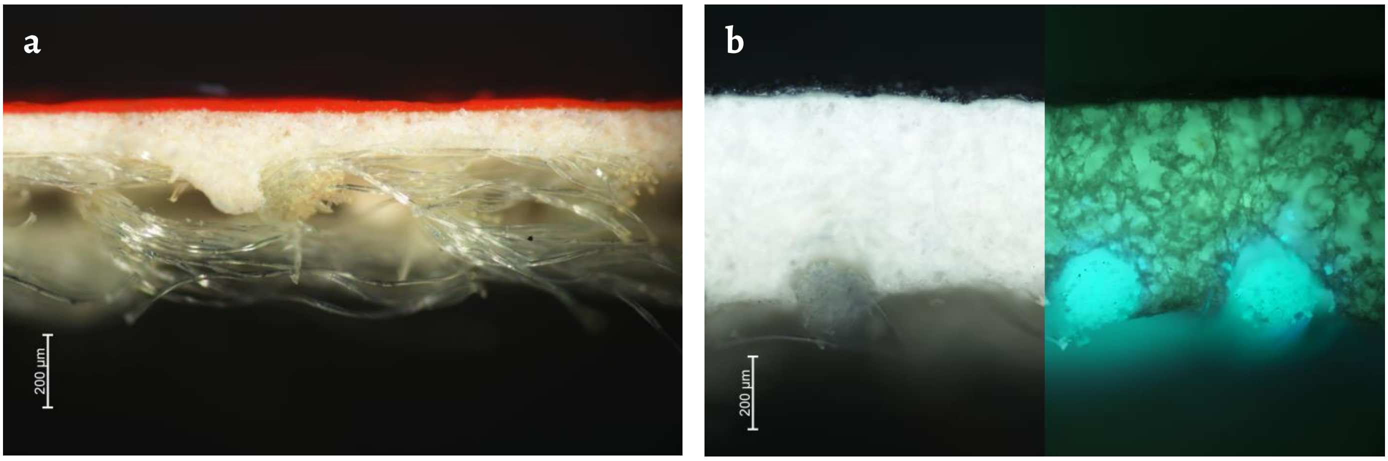


Figure 5. Microscopic images of two cross-section examples of synthetic-coated fabrics (see Table 1) composed of coatings with a microporous structure, possibly produced by the coagulation method: *a)* sample one under cross-polarized visible light; *b)* sample two under cross-polarized visible light (left) and blue-violet (right) radiation.

These microporous-coated fabrics might have been produced by the so-called coagulation process, in which polyurethane is the preferred polymer to produce breathable fabrics and imitations of leather [2, 4, 52]. This procedure can be performed through a direct or transfer coating method and polyurethane can be coagulated by a wet or dry procedure. The principle of the wet coagulation technique is solvent exchange: the TPU, non-soluble in water, is dissolved in a water-soluble solvent, such as dimethylformamide (DMF), followed by an aqueous treatment for the dilution/extraction of the organic solvent, resulting in a progressive phase-separation and subsequent precipitation or coagulation of the TPU and formation of pores [2, 4, 51]. The addition of additives, such as pigments, is particularly difficult with this process since they might also be removed during the solvent extraction step [2]. On the other hand, phase-separation and coagulation of the TPU can also be achieved through the dry-coagulation method or thermocoagulation, based on the controlled evaporation of the solvents in which the TPU is dissolved, in this case commonly a mixture of methylethylketone/toluene in water [2, 4, 51]. Additional layers might be added to the top of the coagulated TPU to impart colour or other properties through the conventional transfer coating method.

The observation of the examples in Figure 5, particularly the lack of pigmentation of the microporous coating and its penetration within the weave of the fabric, indicates that the TPU coating might have been directly applied to the fabric.

Some of the analysed samples also showed coatings with microporous-like structures that seemed to have a composite nature, as indicated by the difference in fluorescence intensity observed under ultraviolet radiation (Figure 6). These layers might correspond to a nonwoven fabric, composed of different fibre types that fluoresce differently, flame laminated to the fabric substrate and coated on top with a polymeric compound, possibly by the transfer coating method. Other possibilities, particularly the ones in which impregnation of the coating into the substrate is observed, might be for the coating layer to be composed of a mixture of polymer resins or of a polymer resin, such as TPU, filled with heterogeneous fibre particles, the latter also identified by Meyer et al. [53]. However, further characterisation of these samples is needed to better understand their composition.

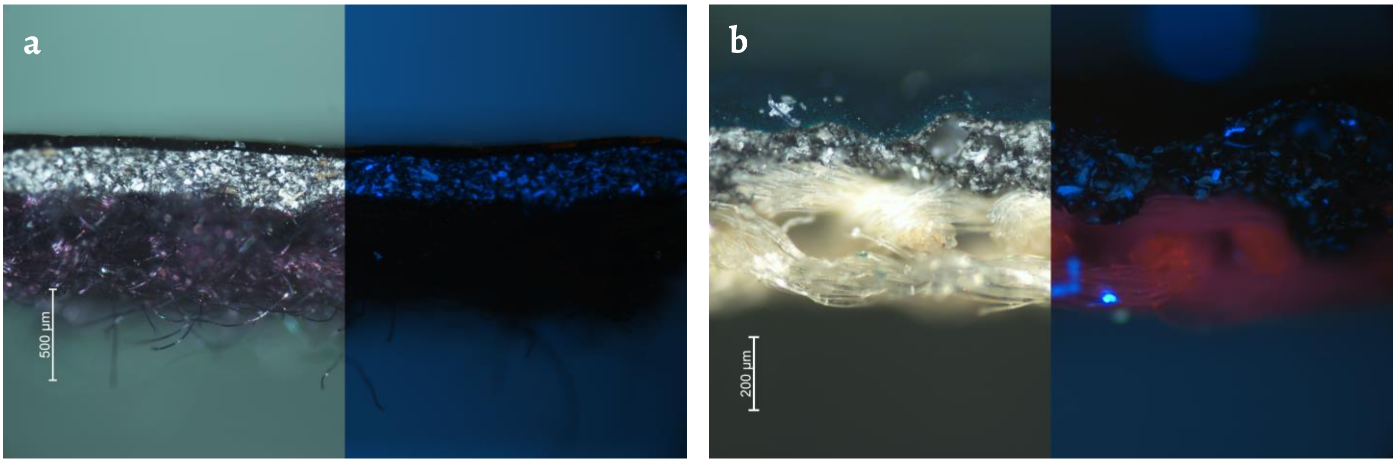


Figure 6. Microscopic images of two cross-section examples of coated fabrics (see Table 1) composed of coatings with a microporous structure, possibly composed of a nonwoven fabric laminated to the substrate or of a mixture of resin/resin or resin/fibre particles: *a)* and *b)* under cross-polarized visible light (left) and ultraviolet (right) radiation.

Flaking and peeling patterns: preliminary observations on TPU-coated fabrics

Flaking and peeling have been reported as common deterioration patterns in synthetic coated fabrics found in museum collections, leading to drastic visual changes and the eventual complete loss of the affected items [8-9]. A brief definition was presented by França de Sá et al. to describe both damages [8], though there is still a lack of knowledge on the possible causes for their occurrence.

In a coated fabric, both peeling and flacking are characterized by a delamination phenomenon caused by a bonding failure. In the case of peeling, the coating layer(s) completely detach in large fragments, while mostly maintaining their overall flexibility. On the other hand, flaking is usually preceded by cracking, leading to fragmentation in smaller-sized pieces of the coating layer(s), resembling small islands, and their subsequent detachment.

The set of analysed samples from items affected by flaking and peeling was only composed of TPU-coated fabrics. In most cases, the delamination observed in both damage patterns occurred at the interface between the coating layer and substrate. However, it is also described in the literature that interlayer delamination might also occur, i.e., separation at the interface between two coating layers due to, for example, insufficient heat during application [4].

As previously described and exemplified in Figure 1a and Figure 3c, flaws in the bonding between the coating and substrate, i.e., areas of no contact, can be weak points in the structure of the coated fabric that are more prone to damage [47]. Humidity might be trapped in these voids, promoting the chemical deterioration of the coating at this interface, which can lead to delamination. The larger the weak point, the more extended the delamination between the layers: large weak points might lead more likely to peeling, while smaller weak points might lead to flaking instead. In addition, due to the composite nature of the coated fabrics, variations in humidity might also cause a differentiated expansion/contraction of the several layers, promoting the delamination phenomenon.

Peeling was mostly observed in thin-coated fabrics with a 2-layer construction (Figure 7), i.e., composed of only a coating and fabric substrate layers. As observed in Figure 7a, it was also noted an overall reduced contact between the coating and fabric layers, suggesting a production through the transfer coating method, as the direct one would have led to an increased impregnation of the coating [3-4]. However, the lack of an adhesive layer to ensure proper bonding between the two layers resulted in a large weak point at this interface and consequent delamination of the coating in large pieces.

On the other hand, flaking was detected in both thin and thicker coating layers on the set of analysed fabric samples (Figure 8).

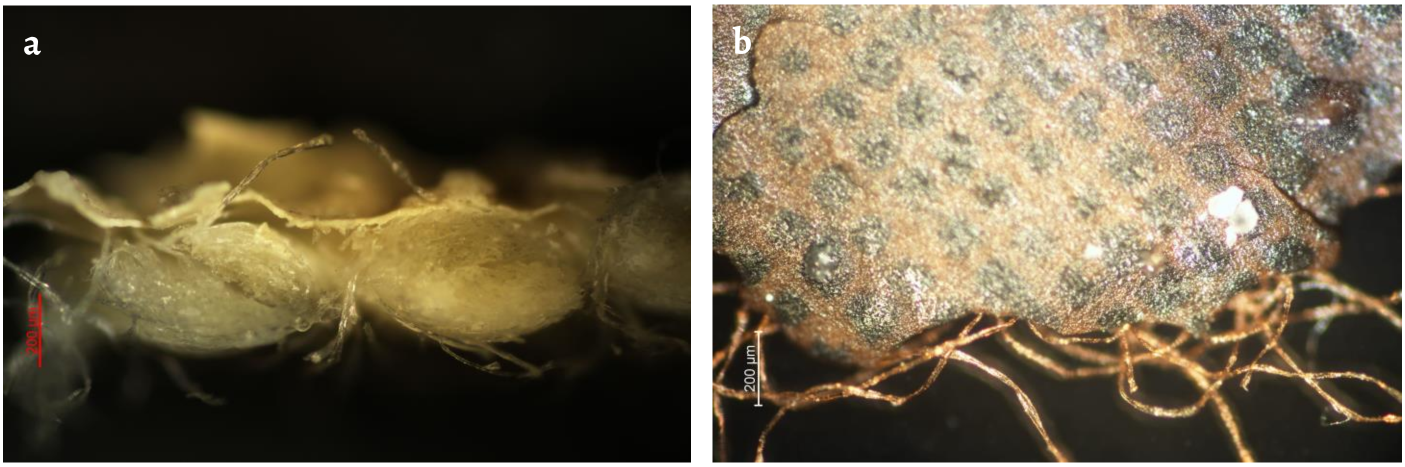


Figure 7. Microscopy images of two examples of thin-coated fabrics (see Table 1) damaged by peeling under darkfield visible light: *a)* cross-section; *b)* top-view.

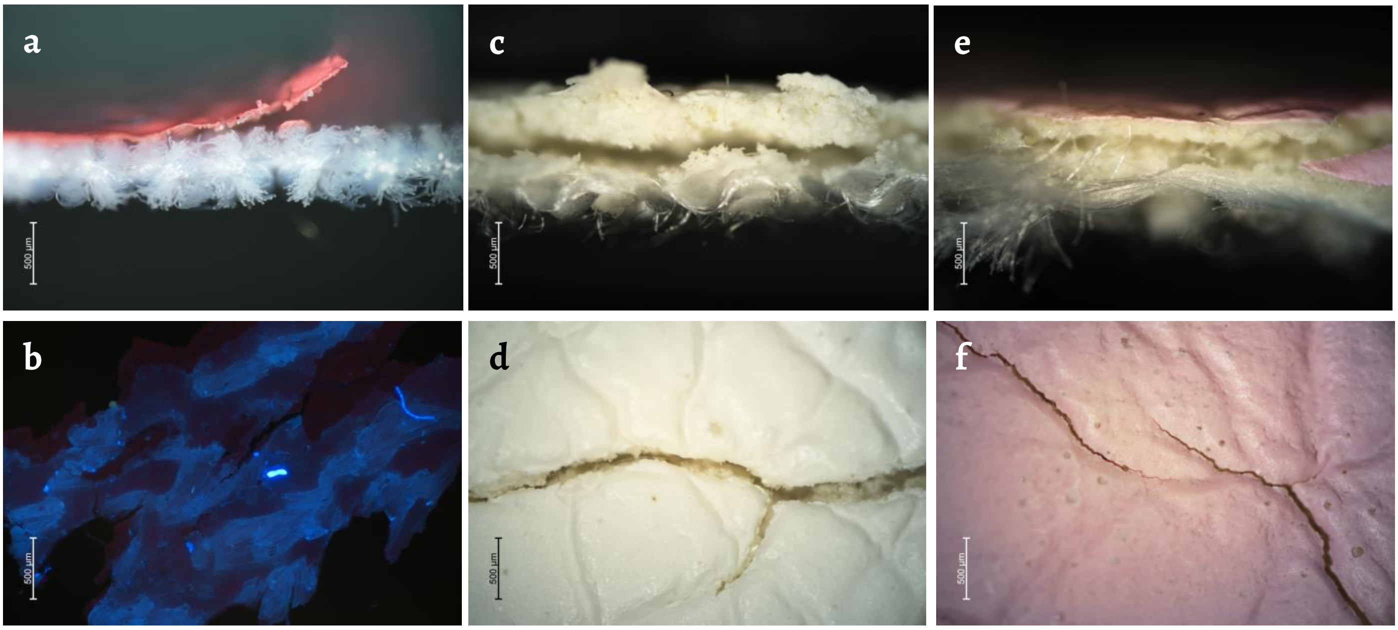


Figure 8. Microscopy images of three examples of synthetic-coated fabrics (see Table 1) damaged by flaking: *a)* cross-section under cross-polarised visible light and *b)* bottom side of the top coating of the same sample under ultraviolet radiation, in which traces of an adhesive layer are visible; *c* and *e)* cross-section and *d* and *f)* respective top-view of two coated fabrics with leather-like textures under darkfield visible light.

Opposingly to peeling, most fabrics with thin coating layers showing flaking were composed of an adhesive intermediate layer (Figure 8a-b). The improvement of the bonding strength between the coating and fabric substrate possibly prevented the detachment of the coating in large fragments. However, the cracking and detachment in smaller fragments does not seem to have been completely prevented by the presence of this adhesive layer, as it might not be homogeneously spread, as the example observed in Figure 8b (corresponding to the bottom of the top coating from the sample shown in Figure 8a), leading to only a partial bonding and areas of no contact between the layers. Extensive physical handling and/or wear of an item might also promote flaking, as it leads to mechanical damage like cracking and subsequent detachment of the broken fragments. In addition, the chemical deterioration of a TPU coating, mainly caused by hydrolysis for the ester-based and photooxidation for the ether-based [54], might also promote cracking of the material, due to internal breakage of chemical bonds that weaken its cohesion and integrity.

Flaking was also found in thicker TPU-coated fabrics, composed of microporous structures and leather-like textures (Figure 8c-f). In these examples, the cracking phenomenon leading to flaking also seemed to have been promoted by the texture of the coated fabric, as the net of embossed grains created a path for a facilitated spreading of a net of cracks throughout the entire surface of the coating, especially the deeper the embossing (Figure 8d and Figure 8f).

Conclusions

The present study reported for the first time the variability of p-PVC and TPU-coated fabrics in fashion museum collections. The construction and morphology of the layers of a selected set of samples were investigated through a straightforward methodology mainly based on a visual assessment by optical microscopy, complemented by infrared spectroscopy (ATR-FTIR) for the identification of material composition. Visual clues were found that enabled the indication of the manufacturing processes used in the production of the coated fabrics analysed. In addition, preliminary results of the detailed observation of delamination damages, namely flaking and peeling, suggest their connection to production methods.

The analysed set of samples showed great variability in terms of the number of layers, thickness, transparency, colour, and morphology. The most common number of layers identified were two and three-layer constructions, composed of a fabric substrate coated with one or two coatings, respectively. In addition, it was possible to identify different coating morphologies, such as compact and microporous structures. The latter are characterized by the presence of a cell structure which can be further divided, depending on the size of the cell, into foamed (bigger size) and coagulated coatings (smaller size). Microporous structures can also be achieved by other means, such as a nonwoven fabric or a composite coating layer comprising a polymer resin filled with fibre particles.

Several methods are described in the literature to produce a coated fabric, but only the distinction between a direct and indirect application of a coating to the fabric substrate was considered relevant for the present study. Coated fabrics produced by the direct coating method usually result in coatings that sink into the weave of the fabric, which can be easily identified when observing a cross-section, that can have either a compact or microporous structure. For this reason, this method is usually not suitable for open-structure fabrics, such as knitted ones, unless a foamed or coagulated coating is applied. On the other hand, coated fabrics produced by the indirect coating method, also known as transfer coating, tend to show a well-defined coating layer that does not sink into the fabric since it is usually in a film form when laminated to the substrate. Intermediate adhesive layers are frequently present in coated fabrics produced by this method. In addition, it is important to highlight that the production of coated fabrics might not be restricted to one method only and that several techniques can be applied to obtain the desired final product.

Fluorescence microscopy proved to be particularly useful in the detection of additional layers with distinctive fluorescence, namely the TPU intermediate layers added for adhesive purposes. The finer resolution of these images also allowed for a better understanding of the morphology of the coatings, particularly of coagulated structures, which helped determine production methods.

Delamination issues, such as flaking and peeling damages, were investigated in TPU-coated fabrics and preliminary results show a connection to the production methods of the materials. Peeling seems to be particularly common in coated fabrics with two-layer constructions, i.e., with no adhesive layer, produced by the transfer coating method. The reduced contact between the coating and substrate layer leads to a large weak area at this interface, causing their separation in the long term. On the other hand, flaking seems to be a more complex delamination phenomenon in which several factors might play a role. It is usually preceded by cracking, which can be caused, individually or in combination, by the physical handling and/or wear of the material and the chemical deterioration of its coating. Although coated fabrics with flaking tended to show a better bonding strength between coating and fabric than the ones with peeling, flaws at this interface were still found, i.e., areas of no contact or voids, which are possibly more prone to physical and chemical damage. These voids are weak points in the structure of the fabric where cracking, followed by delamination by flaking, might be more likely to occur. Additionally, coated fabrics with leather-like textures seem to be particularly prone to flaking, as the net of embossed grains seemed to create a path for a facilitated spreading of a net of cracks throughout the entire surface of the coating.

It was also concluded in this research that it is not possible to distinguish p-PVC and TPU-coated fabrics merely through visual assessment, which highlights the need for further molecular analysis for proper identification of the material. However, the present study proved the value of a simple observation-based approach for a first assessment of the synthetic-coated fabrics present in fashion museum collections. The detailed observation of the subtle differences in their structure and morphology contributes to the increased knowledge about these materials which will hopefully pave the way for the development of informed and suitable conservation strategies for their long-term preservation.

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Real or faux leather? Luxury or ready-to-wear mass production? Characterization of three TPU shoe coatings (ca. 1970) from the Kunstmuseum Den Haag fashion collection

Pele ou imitação de pele? Luxo ou produção em massa de pronto-a-vestir? Caracterização de três sapatos revestidos com TPU (ca. 1970) da coleção de moda do Kunstmuseum Den Haag

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Abstract

During the 1970s, the shoe industry's transition from real to faux leather raises questions about transparency regarding the materials used and the real cost of the production. Were luxury brands conscious of the quality of the products that they offered consumers, compared to other ready-to-wear market brands? Or, on the other hand, were they simply following trends in the fashion industry made possible by the introduction of leather substitutes? By studying three different shoes from the Kunstmuseum Den Haag's fashion collection, a comparison can be drawn between the products used by well-known luxury fashion brands such as Charles Jourdan or Gucci, and those used by lesser-known brands for mass production such as Valentina. The results obtained by analytical techniques (OM, SEM-EDX, ATR-FTIR) reveal similarities between the both luxury brands and the mass-production brand as well as similar degradation elements.

KEYWORDS
Thermoplastic polyurethane (TPU)
Charles Jourdan
Gucci
Adipic acid
SEM-EDX
ATR-FTIR

Resumo

Durante a década de 1970, a transição da indústria do calçado de pele verdadeira para pele sintética originou questões sobre a transparência dos materiais utilizados e o custo real da produção. Estariam as marcas de luxo conscientes da qualidade dos produtos que ofereciam aos consumidores, em comparação com outras marcas de pronto-a-vestir? Ou, por outro lado, estariam estas marcas apenas a seguir as tendências da indústria da moda possibilitadas pela introdução de materiais substitutos da pele natural? Através do estudo de três sapatos da coleção de moda do Kunstmuseum Den Haag, foi possível comparar os materiais usados por marcas de luxo famosas, como Charles Jourdan ou Gucci, com aqueles usados por marcas menos conhecidas, de produção em massa, como Valentina. Os resultados obtidos com diferentes técnicas analíticas (OM, SEM-EDX, ATR-FTIR) revelaram semelhanças entre os materiais das marcas de luxo e das marcas de produção em massa, bem como padrões de degradação semelhantes.

PALAVRAS-CHAVE
Poliuretano termoplástico (TPU)
Charles Jourdan
Gucci
Ácido adípico
SEM-EDX
ATR-FTIR

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Introduction

Throughout history, fashion and clothing have been influenced by the intersection of technology, craftsmanship, and materials. Over the span of 2000 years, traditional materials like textile fibres and leather have been combined with contemporary practices, including advancements in the chemistry industry such as the discovery of polymers [1]. Many of these innovations have been driven by the desire for increased comfort, practicality, protection, exclusivity, or other priorities. Before early industrialization in the nineteenth century, the concept of "exclusivity" was limited to the upper classes and was determined by the rarity of materials used, labour, or craftsmanship invested in the product. However, with the introduction of new technologies and materials, concepts of exclusivity began to evolve. New materials reduced the investments of time and craftsmanship, eliminating the lengthy tanning processes characteristic of leather production in the past. This was not a new process since treating fabrics with special oils to achieve similar appearances as leather was already seen centuries before [1]. Japanese lacquers, for instance, were brought into Europe during the nineteenth century and traded in international exhibitions, showing their strong waterproofness and resistance to wear [2]. Were those inventions the forerunners of the modern patent leathers that inspired the European industries? Traditionally, patent leathers are applied to upper leathers from goat and calf skins [3]. The leather substitutes were made originally by soaking natural fibres such as cotton in natural resins or waterproofing with lacquers, years later the technology evolved fabricating foils or plastics films coated over substrates [4]. Engineers and chemists now played a larger role in the creative process, working with machines, rather than relying solely on the artisan's handiwork. From those experiments, new range of materials were born revolutionizing the clothing and fashion [4]. The discovery of vulcanization in natural rubber (creating products such as "leathercloth") or later on by combining semi-synthetic polymers such as cellulose nitrate (Fabrikoid) brought new alternatives into the market [5]. The presence of nitrocellulose during the 50s became a common material for patent finishes [3]. However, all those new products did not accomplish the main qualities of leather, such as endurance, flexibility, and breathability, aging very badly due to their inherent instability [6]. These experiences led the polymer industry to further research for improving previous materials. During those years, other variations were tried with vinyl fabrics that were coated with polyvinyl chloride (PVC) [7]. From those experiments, products like Naugahyde were born. Unfortunately, the material did not breathe as expected and created very hot and tacky feet [1]. This fact did not exclude the presence of PVC or polyurethanes. Their presence in modern society became an alternative to real leather, advertising its use as a contemporary solution for luxury brands. Popularly known as "pleather" (synthetic leather made with a plastic coating) it was sold under different brand names [4]. This shift was sustained by the increase in official patents filed after the 1950s [8-10]. Among numerous manufacturers, DuPont, Toray, and Kuraray were undoubtedly the most productive until the end of the century, developing products such as Corfam and Clarino, just to mention few [1]. DuPont learned, after the bad experience with PVC coatings, the importance of developing the breathability aspect in order to ensure more comfort [1]. Corfam was their first improvement, quickly implemented into production for work safety shoes in America. This success echoed the fashion market by shoe producers like Ferragamo, Andrea Pfister Patou (1971 spring/summer collection), Roger Vivier who designed for Mme Grés and Yves Saint Laurent in 1969 or Mabel Julianelli, among others [4, 11, 12, p. 19]. It is somehow surprising to see advertisements promoting Corfam as an excellent product and the most up-to-date alternative to genuine leather. However, very little was said about its production process, its components, or the reduced need for human labour due to the introduction of new machinery. The marketing strategy solely focused on the success of the new products and their low production costs [4]. Throughout the 1970s, *Combat (le Journal de Paris)* and other local newspapers covered ongoing protests against these changes by shoe workers in the leather industry, particularly at French factories such as the "Romans" where the Charles Jourdan luxury line Seducta was produced [13, p. 7, 14, p. 2]. Over time, Corfam and other Thermoplastic polyurethane (TPU)-based materials did not meet expectations, showing rapid decay and poor aging [15]. The experience in creating these inventions led to the development of new types of synthetic leathers, and other companies also attempted to adapt this knowledge to create their own synthetic by-products. However, the presence of leather was not totally banished, since, as will be proven in this research, the presence of this genuine material was still in use alone or in combination. The substrates (made of natural fabrics or synthetics and even leathers) were coated equally following identical processes, although the final products were not always described as faux leathers.

Case studies

Three pairs of shoes from the Kunstmuseum Den Haag fashion collection (KMDH) were chosen for this study. The first two designs, by Gucci and Charles Jourdan (Figure 1), originally belonged to luxury brands. Starting with the Charles Jourdan shoes (KA-32-1986 1.2) the company founded in 1919, it was specialized in women's shoes using meticulous workmanship and exquisite materials. After the Second World War, they produced shoes exclusively for the House of Dior until the 1960s when they began new collaborations with other French fashion houses such as Givenchy, Yves Saint Laurent, Pierre Cardin, Pierre Balmain, and Emanuel Ungaro. These collaborations were led by highly respected artists like Andrée Perugia, T. Elliott and Sons, Karl Lagerfeld, and Roger Vivier [16, p. 56, 17, p. 3]. The shoes from the KMDH collection reflect the characteristic Louis XV or Charles IX heel in silver colour with silver embellishments and became an internationally recognizable model following a 1970s collaboration with French photographer Guy Bourdin. Victoria & Albert Museum in London (T.108-2012) and The Costume Institute in New York (1972.27.12 a.b.) conserves very similar shoes in their collection [18-19].

The second pair of shoes corresponds to the Gucci's (KA-5-2015 1.2) (Figure 1), which were known at the time as "loafers". Originally sold in various colours and advertised as real leather, comparisons with identical pieces from other collections, such as those in the V&A collection (T.693:1-2000), showed barely any degradation problems as Elizabeth-Anne Haldane Lead textile conservator from V&A confirmed during this research [20]. Featuring the characteristic gilded logo on the tongue and inspired by horse racing outfits, the first loafers designed by Aldo Gucci in 1953 had a significant global impact and were worn by well-known figures, including actresses such as Ava Gardner during the presentation of *Mogambo* in the same year [21, p. 181, 22, p. 5]. The Italian shoe company, like Charles Jourdan, had a long history of specializing in leather and luxury goods since its establishment in Florence in 1921. The shoes conserved in the KMDH collection are characteristic of the pilgrim-style pumps with squared toes and low, broad heels popularized through Yves Saint Laurent and Roger Vivier's iconic 1962 designs.

In the 1970s, both companies underwent a significant transformation with the introduction of ready-to-wear products marketed as "ready-to-wear de luxe" [16, p. 184]. Charles Jourdan defended the inclusion of these products in their collections, claiming that it did not imply a reduction of their quality and maintaining the brand's luxury reputation by assuring their clientele of high standards. After the 1970s, the American brand Genesco became the majority shareholder of the Charles Jourdan group. Whether this had any impact on the quality of their products compared to previous years is unclear, but by this time, the family business was run by the three sons of Charles Jourdan: René, Charles, and Roland. They brought innovation to their work by using new materials and technology in the production. In contrast, Gucci seems to have maintained the traditional methods for which the house was known, using two pieces of leather for the upper part, hand-painted with water-based products, waxed, and finally hand-stitched together [21, p. 181].

Figure 1. Analysed shoes and samples taken seen under stereomicroscope (red: sample a, and blue: sample b): *a)* Gucci (KA-5-2015 1.2.); *b)* Charles Jourdan (KA-32-1986 1.2.); *c)* Valentina boots (KT-27-1984 1.2).

Figure 2. Boots: *a)* Mario Valentino boot (KA-12-1984); *b)* Valentina boot (KT-27-1984 1.2).

The third pair of shoes in this study, corresponded to a pair of boots by Valentina (KT-27-1984 1.2- and less familiar in fashion history) (Figure 1), which showed values commonly seen in shoes destined for a broader mass market. The boots exhibit a style that was very popular during the 70s and show close similarities to those made by Mario Valentino and other well-known Italian shoe producers, and more broadly to numerous models across the Italian mass-market. The similarities may be coincidental but seem obvious when looking at the colour choices, as well as the logo placement at the heel (Figure 2). However, these similarities seem to be primarily aesthetic. A comparison with Valentino boots from the KMDH collection (KA-12-1984 1.2) demonstrates differences in finishing as well as in product quality (Figure 2). The Valentino boots highlight the use of real leather, whereas the Valentina appear to be made from different materials (despite the leather logo on their sole). At least two different substrates are apparent: a very strong one to maintain the shape of the boot, and another softer substrate providing flexibility to the middle section.

Production of synthetic leathers

A cross-section of early synthetic leather reveals a substrate, an interlayer material used for reinforcement (possibly textile or even foam), followed by a compact layer and a topcoat [23]. It is from these textile, foam, or leather substrates that these new leathers develop their own characteristics and their similarities in flexibility with genuine leathers [24-25]. Many case studies have examined the types of coatings used in fashion since the 1950s (particularly with PVC and TPU), as well as their causes of degradation [26]. Focusing solely on TPU, originally produced by diisocyanates (aromatic or aliphatic) and polyols (ester or ether-based) – two of the most important families of polyurethanes – very little has been found in the conservation literature about the sorts of substrates to which those synthetic coatings were applied [7].

Official patents indicate that substrates underwent highly developed and complex processes. While similar processes were generally carried out for the surfaces (by impregnation, direct, or transfer coating), the substrates underwent other manipulations [27-28]. The aforementioned Corfam, with its non-woven substrate, was one such material first adapted for the fashion world [1]. These non-woven fabrics were revolutionary compared to woven textile substrates, as their combination with polyurethane ensured higher flexibility and breathability, making them the perfect material for shoe uppers [29]. Their success was based on several factors, starting with the development of bicomponent fibres, which are created by mixing two immiscible polymer types (polyester/polyamide) and resulted in new kinds of fibres named side-by-side fibres, segmented fibres, or sheath-core fibres [28].

The differences between these new fibres were based on their core and on the number of fibres that one sole thread was able to create, offering higher water penetration and release of perspiration. The material was compressed and shrunk by submitting these bundled fibres to felting techniques, using needle punching in combination with warm baths [28]. The resulting non-woven substrates were impregnated with polyurethane resin, binding the fibres together [30]. The second major advancement in these revolutionary substrates came some years later with the introduction of multicore fibres. These new fibres had improved water-wicking properties, and fibre thickness was refined from 0.5 to 0.0001 deniers [31]. This new achievement was made possible through the process known as “island-in-the-sea”, where the synthetic fibres (the island) and the polymer (the sea) were combined, creating very fine flexible fibres [32].

The next stage in artificial leather production was the possible addition of a fine layer of adhesive to secure the interlayers [1]. Because non-woven substrates did not take up the top coatings evenly, as evidenced by issues with Corfam, new patents were developed integrating an additional textile or foam (interlayer) between the substrate and the surface coating. This was confirmed by numerous patents focused solely on the breathability of those leather-look-like sheets [33-34]. Patented substrates Hitelac (1965) and Clarino (1966) showed considerable improvements. Clarino, for instance, embedded fibres within polyurethane foam, improving surface bonding with the top coating. These fibres did not adhere to the foam but moved freely through a “tunnel system”, a process achieved by the coagulation of polyurethane with dimethylformamide, resulting in the microporosity characteristic of natural leather [35].

Degradation of the coatings

All three shoes showed signs of degradation, presenting abrasions, cracks, deformations, and even a coating surface change from glossy to matte. The most visible degradation was the systematic presence of a characteristic white surface over the coatings, known as blooming commonly used in conservation of plastic [36, p. 271] (Figure 3). This could be seen in a cloudy form or even as crystals in the form of efflorescence. In synthetic coatings like TPU, PVC, or cellulose nitrate, this is a direct consequence of polymer degradation [4, 6]. In TPU-based polymers, this has been previously identified as acid, with adipic acids being the most commonly reported so far [15]. In PVC or cellulose nitrate, other components have been identified – from hydrochloric acid to palmitic acid, stearic acid, or azelaic acid – in previous research [4, 6-7]. Leathers can sometimes also show a white surface due to oil-based dyes, which may be exacerbated by the formation of fatty acid spews. This reaction creates a characteristic white surface, especially if the leather is dressed and stored in cool climate conditions [37, p. 115]. This was confirmed by Conservator Fran Ritchie [38] who treated a 1930s jacket from National Park Services History Collection (1145) which showed a completely white surface by the consequence of using a leather dressing such as neatsfoot oil or saddle soap [39, p 18].

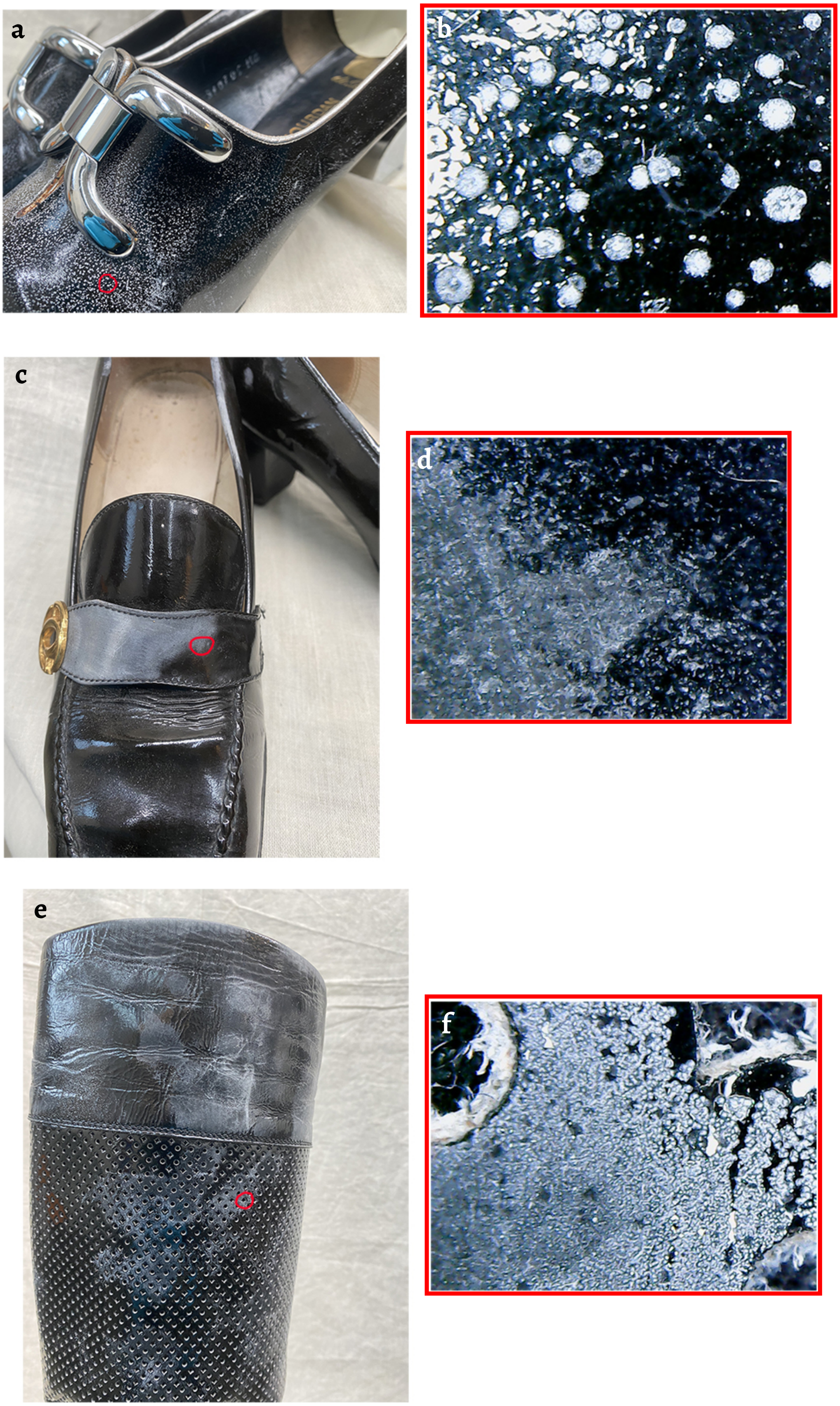

Figure 3. Degradation elements seeing in form of blooming at the three shoes from this research showing a diversity of forms, from a sort of crystals to a cloudy form. Shoes and the details (red) studied with Dino-Lite: *a-b)* Charles Jourdan, *c-d)* Gucci; *e-f)* Valentina.

The shoes analysed for the study reflect the 1960s fashion trend of wet-look patent leather with a glossy finish; however, their original black glossy coating surface is now mostly matte, with some areas of gloss remaining [27]. This change is a consequence of the coating's degradation [7-8, 23, 40-41]. Traditionally, this gloss has been achieved by a heavy topcoat application, formulated with linseed oil, pigments, fillers, binders, resins, polyurethanes, crosslinkers, and solvents [42].

Additionally, the three objects showed signs of having been worn before they entered the collection, presenting material deformation visible on the sole and surfaces. The aforementioned degraded coatings indicated a potential presence of synthetic coatings (TPU or PVC), especially considering the chronology of all of them, since from the 1950s onwards the presence of synthetic coatings was a usual process in the shoe industry. Leather was, of course, not forgotten, sometimes combining both technologies together.

Research aims

This study, therefore, aims to reflect the significant changes in the synthetic leather industry after the 1960s, characterizing the coating and layering of various substrates used to imitate leather surfaces. The three subjects were identified as suitable candidates for sampling, as they were all produced during this period of technical advancements. Was the creation of the three pairs of shoes based on synthetic polymers? Is the white blooming identified on the shoes caused by leather dressings rather than related to the presence of synthetic coatings? The following sections present the different methods used to examine the three selected objects and to characterize the degradation causes affecting them. The results will be compared to existing literature – official patents from the 1960s onwards – and offer a discussion on where claims to "exclusivity" for those products might lie.

Materials and methods

Different samples were taken from the study objects with visible degradation elements. From Charles Jourdan (KA-32-1986 1.2), two samples were collected, one from the black coating and one from the silver decoration around the edge. From the Gucci (KA-5-2015 1.2), one sample was taken from the upper side of the tongue. Finally, from the Valentina boots (KT-27-1984 1.2), two samples were collected: one from the strong substrate described as "sample b" and one from the soft substrate known as "sample a" (Figure 1). All of them were submitted to different analytical techniques, which have previously provided potential results in other academic research [7, 23, 27]. Due to the lack of scientific equipment at KMDH, it was decided to sample the objects and characterize them at Institut Valencià de Conservació, Restauració i Investigació (IVCr+i) in Spain.

Optical microscopy and scanning electron microscopy (OM-SEM)

Recent research has demonstrated the value of examining stratigraphic sections of modern leathers to understand their composition and manufacturing process [40]. Cross-section and longitudinal sections of the samples were prepared and studied under microscopy, using a Nikon ECLIPSE 80i optical microscope with a Nikon DS-Fi1 camera, equipped with reflected and polarized light with UV illumination. Additionally, a Hitachi S–3400N scanning electron microscope was used in backscattered electron (BSE) mode. The samples were embedded in a silicone mold to create resin blocks using a bi-component resin (Technovit 4004). As a first step, the blocks were prepared with the resin, allowed to dry separate and individually. Afterwards, the samples were embedded in the same resin, cut and polished to obtain a clear cross-section.

Energy dispersive X-ray spectroscopy (SEM-EDX)

The samples were studied using SEM-EDX with a Bruker-Quantax X Flash detector coupled to a Hitachi S–3400N scanning electron microscope. The analysis focused first on the surface and then on the cross-section.

Infrared spectroscopy in attenuated total reflection mode (ATR-FTIR)

A Bruker-Tensor II Fourier Transform Infrared Spectrometer (FTIR) was used in combination with a diamond crystal device (ATR). No prior preparation of the samples was necessary, as the analysis was conducted by direct contact with the glass beam. FTIR has been used in multiple studies to identify TPU and can provide accurate results in identifying polymers and degradation causes [7, 27, 40, 43]. Since the characterization process requires comparing results with existing reference data, some of the samples analysed in this research (particularly the coatings) and the degradation causes were identified with the assistance of Dr. Susana França de Sá.

Results and discussion

Records indicate that up to five interlayers could be added before the application of the final coating sheet is done [30, 33, 44]. Initial interpretation of the sample layers, using comparisons with other studies, suggested a leather or non-woven fabric substrate combined with a foam interlayer beneath a very fine top coating. As all three shoes originally had a glossy patent leather appearance, studying the surface coating under stratigraphy was of particular interest. Some manufacturers were known to add layers of resin before the final printing process [45-46]. To emulate the pores of real leather, polymer surfaces might be punctured with extremely fine needles ranging from one mil (one thousandth of an inch or 0.0254 mm) to ten mils in diameter or buffed with silica, emery, aluminium oxide, or carborundum-coated paper [24]. None of these characteristics were found in the collected samples, which featured a highly homogeneous surface with no additional material. The coating is continuous and even, with good cohesion and no traces of peeling like it was seen under SEM (Figure 4). This high quality was likely achieved through the use of solvent-based coatings [42]. This method was used until 1999, when the European Union imposed strength regulations limiting volatile organic compounds in leather factories [42].

The results from OM of the samples revealed at least three distinct layers, except for the grey sample taken from the Charles Jourdan shoes, which showed only one substrate and one coating layer. The samples indicated a simple structure of one substrate (1), one compact layer constituting the interlayer (2), and one top layer forming the coating (3). Interestingly, the Charles Jourdan shoes exhibited a variation in the interlayer, with the presence of a foam rather than the compact layer seen in the Gucci and Valentina shoes (Figure 5).

The Valentina sample suggested differences in production, particularly at the substrate level, as "sample a" did not show the same characteristics as "sample b" (Figure 1). This variation could be due to the part of the leather used; bovine leather hides, for instance, show a highly characteristic fibre network under the surface grain (corium), resulting in a very flexible material [2]. Given that the sample analysed corresponded to a perforated boot, the addition of a coating may have obscured the fact that the leather was not fully grain. The use of bottom leathers (corium) served purely to reduce costs, which were offset by adding thicker coatings [2]. The use of different parts of the leather has been noted in official patents, such as the use of grain made from split leather [30, 33]. Interestingly, it was noted that the coatings on sample a experienced less blooming than sample b.

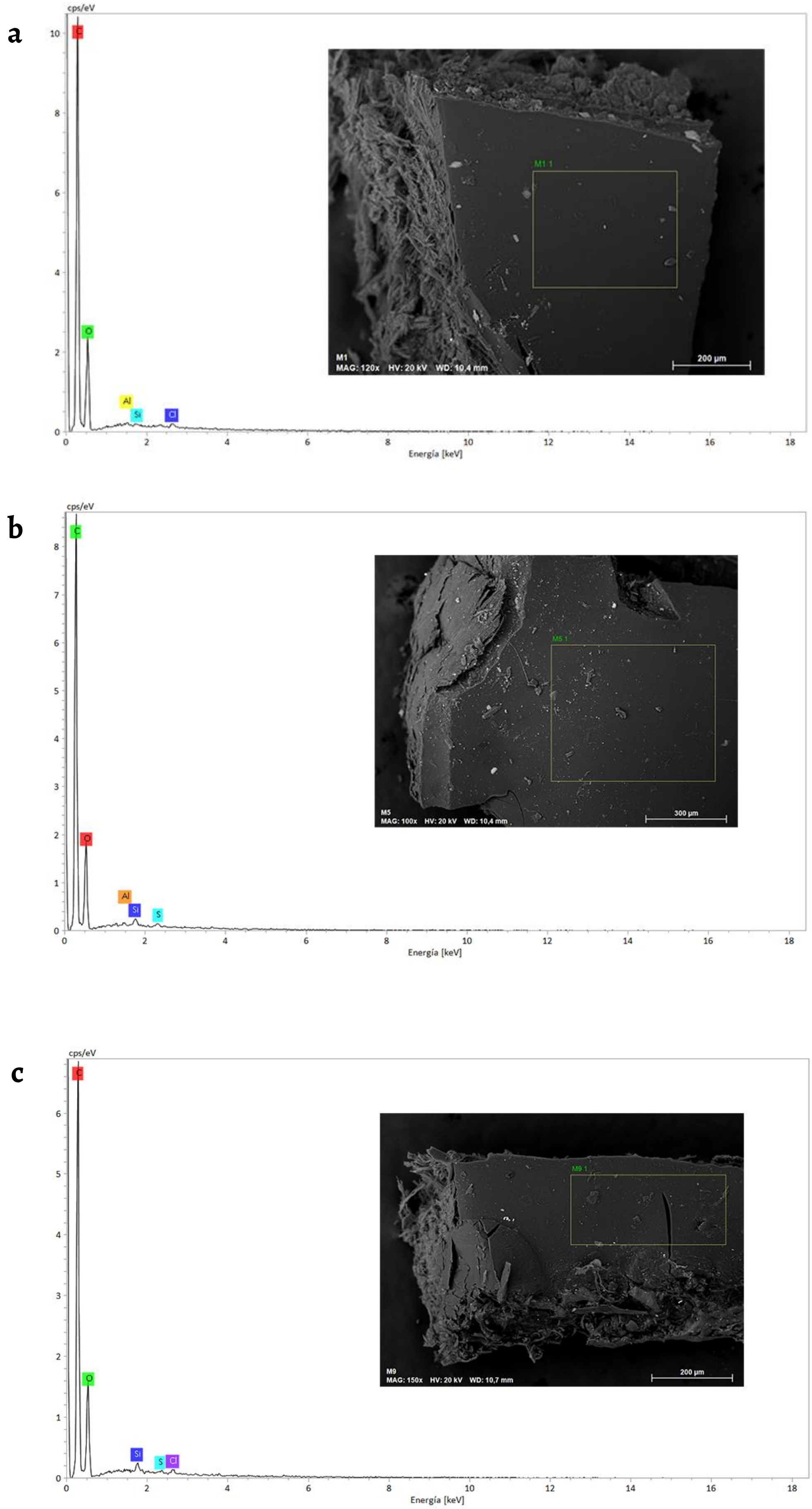

Figure 4. SEM-EDX results carried out over the surface of: *a)* Valentina boots; *b)* Gucci shoes; *c)* Charles Jourdan shoes.

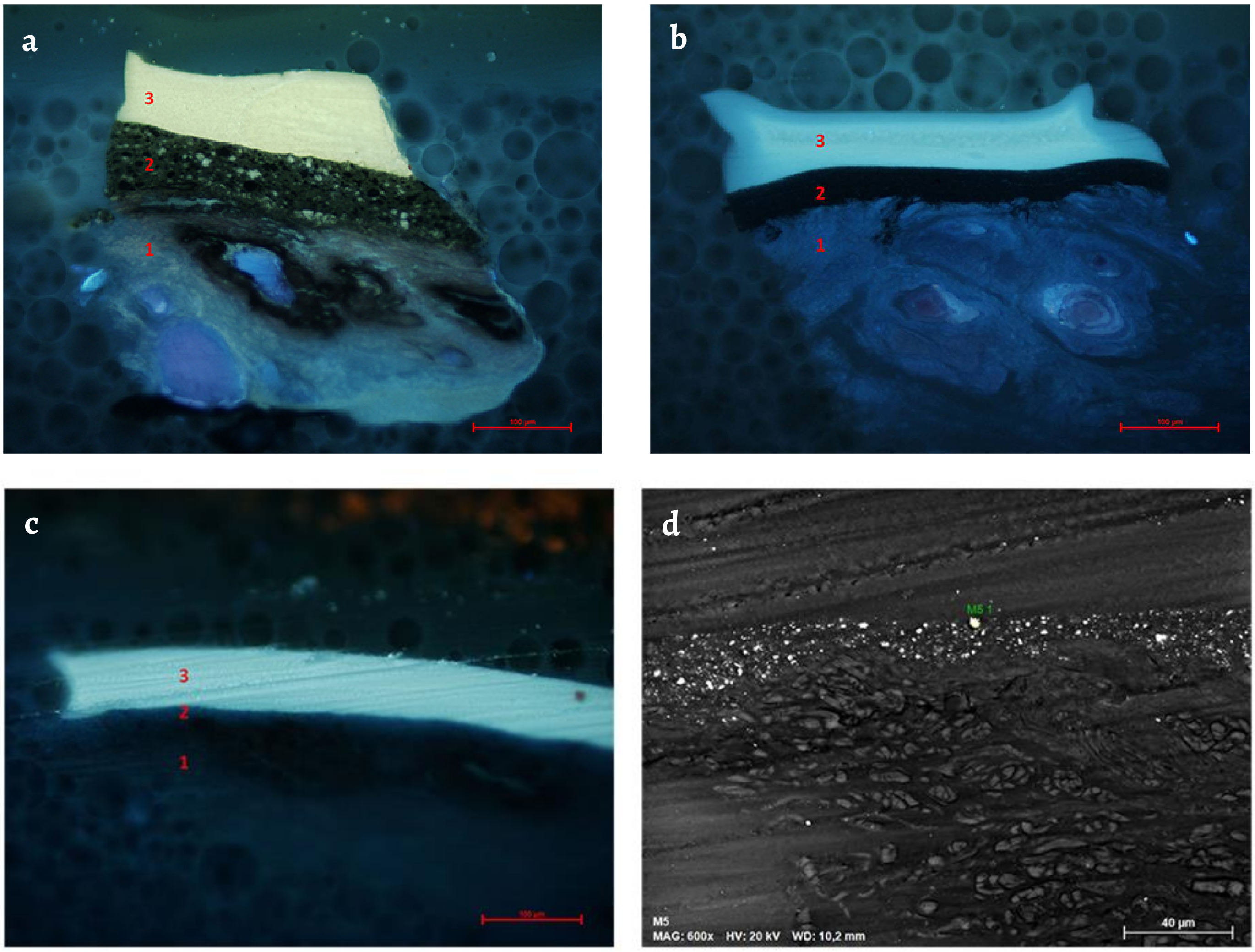

Figure 5. Stratigraphy of the collect samples from: *a)* Charles Jourdan shoe and *b)* Valentina boots, both seen under MO-UV 200×,showing 3 layers in total, differing the interlayer: Charles Jourdan shows a possible presence of a foam layer (2) while the Valentina the characteristic compact layer (2); *c)* Gucci shoe (OM), which did not reveal much substrate; *d)* Gucci shoe SEM microscopy where the characteristic of grain leather was seen.

The grey sample collected from the edge of the Charles Jourdan shoes displayed a different structure from the other samples examined under OM. Beneath the silver coating, a very compact bundle of twisted textile fibres held together by a type of resin (Figure 6).

EDX identified components such as silicon, aluminium, and chlorine within the surface area of the samples, all associated with colouring materials, as well as fillers, plasticizers, and modifiers added to the polyurethane prior to casting [47] (Figure 4a-c). The cross-section analysis revealed additional diversity in results. For example, the black sample from the Charles Jourdan shoes showed traces of chrome with high levels of chlorine (Figure 7a). This could be linked to substrate elements associated with leather production migrating to the upper surface after the manufacturing process. Chrome has been widely used in the tanning industry since its invention in 1884 and is still a common process for treating leather for upholstery, shoe uppers, garments, and bags. It is also used in the production of TPU coatings due to its good bonding properties [29]. Chrome is cheaper than traditional tanning processes for leather and shows greater resistance to crosslinking [1].

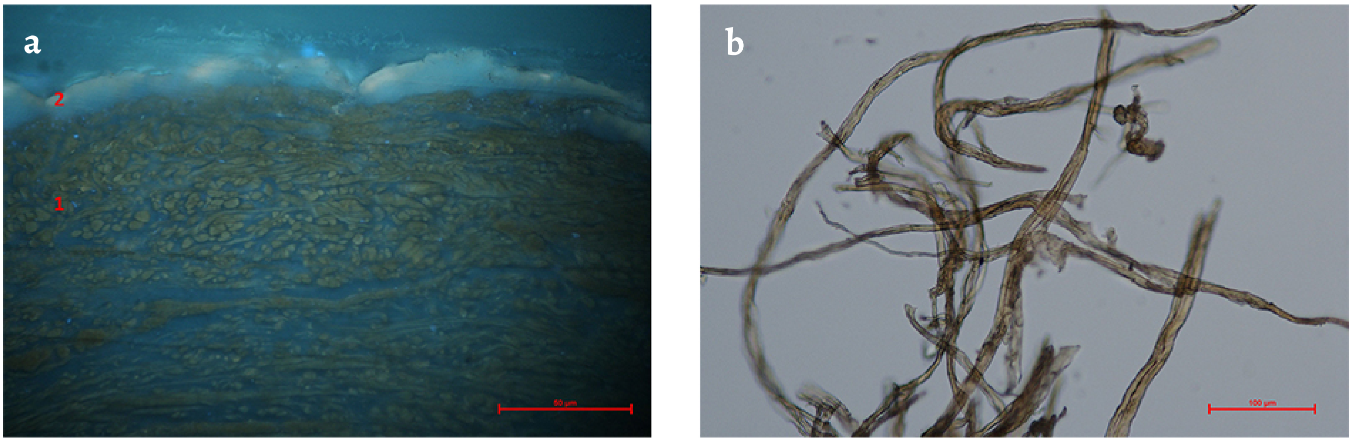

Figure 6. Charles Jourdan shoe: *a)* sample obtained from the silver edge , studied under OM in cross-section in UV mode (unlike the other samples, only two layers are visible; *b)* fibres taken from the substrate showing a slightly twisted core identified as cotton.

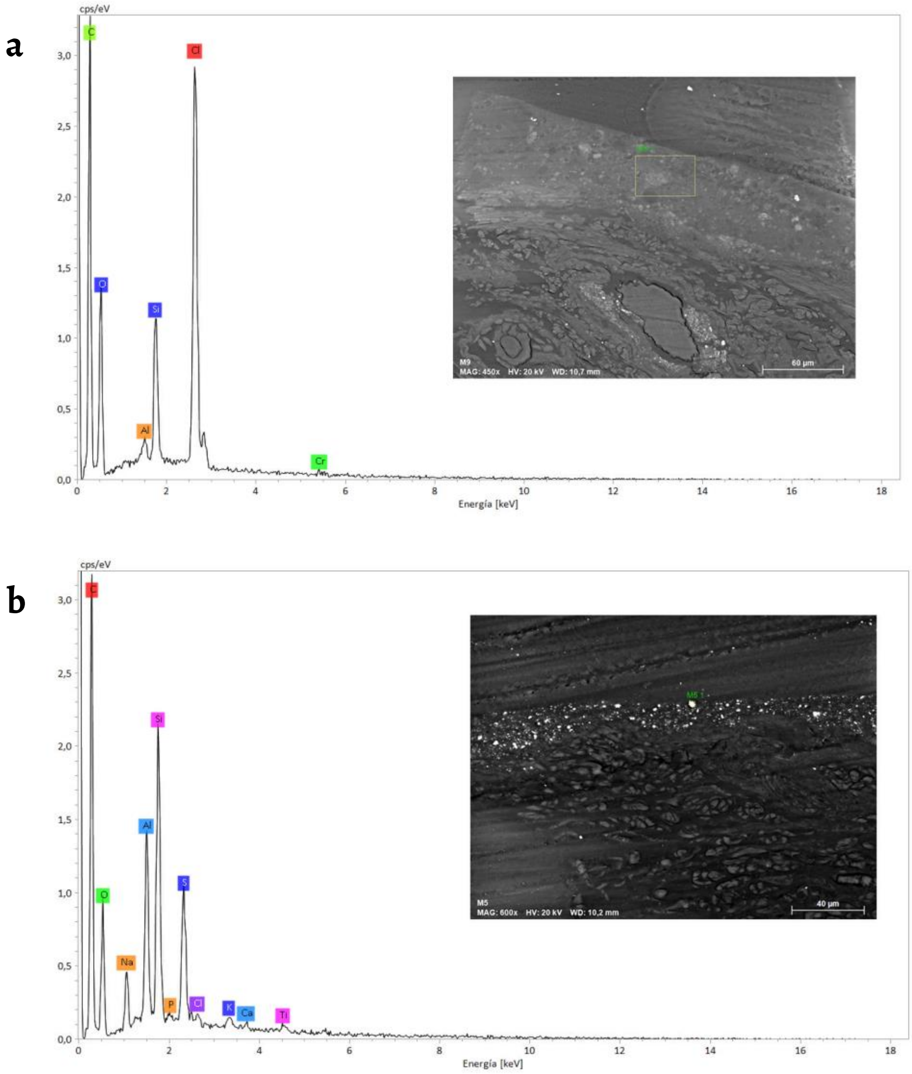

Figure 7. SEM-EDX analysis carried out on the lateral side of the samples: *a)* Charles Jourdan shoes identifying chrome as one of the components on the coating taken from the black sample; *b)* Gucci shoes with the presence of titanium dioxide.

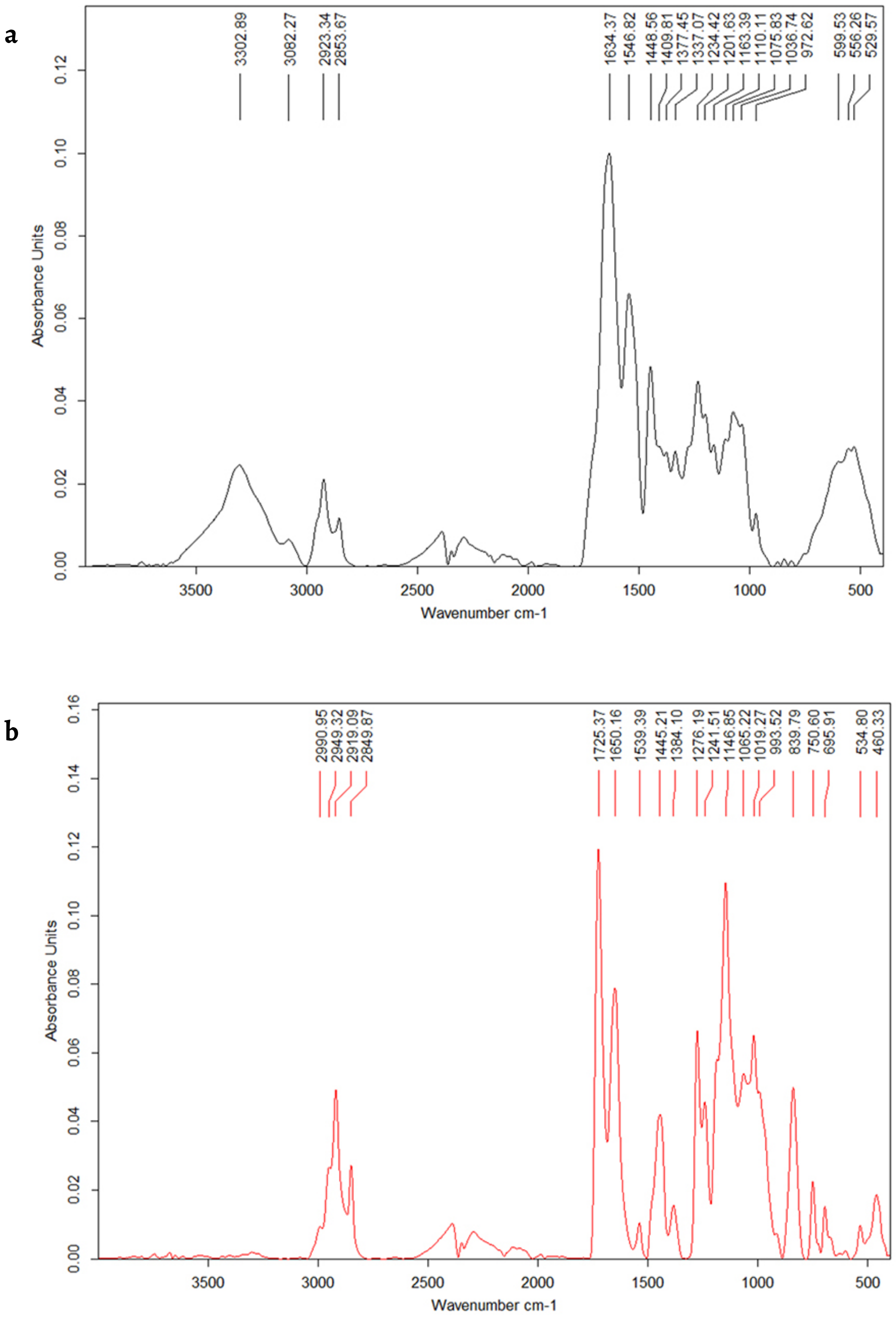

Figure 8. FTIR spectra with the identification of: *a)* nylon by the characteristic wavelengths around 1640 and 3300 cm^{-1}; *b)* the presence of polyacrylic resin by the characteristic bands of 1725, 1445, 1146 and 993 cm^{-1}.

EDX also identified additional components in the Gucci shoes, such as titanium, probably in the form of titanium dioxide (TiO2) (Figure 7b). Used as a white pigment, titanium dioxide is widely used in the coating industry for its ability to whiten and increase brightness or opacity when mixed with dye [48]. Fabrikoid, for instance, replaced zinc oxide with titanium dioxide technology after 1931 due to its higher refractive conditions, creating titanium dioxide pigments [6]. Titanium dioxide exists in two forms – anatase and rutile – with anatase being more effective at scattering light [49]. Its presence in the Gucci shoes was identified as a white crystal in the cross-section, likely added to increase the brightness of the TPU coating.

The ATR-FTIR analysis showed the presence of polyamide (probably Nylon 6, indicated by strong bands around 1640 and 3300 cm^{-1}) and polyacrylic resin in the Charles Jourdan shoes (Figure 8a), where the fibre bundles are bonded together [36, 50, p. 52]. Since the 1960s, the combination of Nylon 6 has been useful in creating bicomponent fibres and manufacturing non-woven substrates, as described in many patents from that time [51]. This finding suggests that these techniques were still in use during the 1970s for the embellishment of Charles Jourdan shoes. The presence of polyacrylic polymer was unexpected, as most official patents consulted suggest the use of other polymers such as PVC, polyurethane, or even cellulose nitrate [9-10] (Figure 8b), all of which have poor aging properties.

The substrates were also examined, and leather was identified as the main material in all samples. This was confirmed through comparison with FTIR leather reference spectra [52]. However, it was not possible to determine the type or quality of the leather used by FTIR analysis alone. The Gucci sample cross-section had insufficient quantities of substrate for full characterization. Observation under SEM indicated traces and similarities in construction with leather structures (grain) seen in other research projects, although this hypothesis could not be definitively confirmed (Figure 5) [53].

Finally, the degradation elements identified as blooming suggested the presence of adipic acid, as indicated by the shift in the C=O stretching band around 1700 cm^{-1}, a consequence of the degradation of the ester-based polyol [7]. This is visible in the Charles Jourdan shoes, which show lower wavenumbers compared to the Gucci and Valentina shoes, especially with the presence of 923 cm^{-1} (Figure 9c). The results confirm the coating's nature as TPU by the characteristic bands around 3330 and 1730 cm^{-1}, ruling out other synthetic polymers or leather dressings. Previous studies have differentiated between aliphatic and aromatic isocyanates in TPU by examining wavelengths between 1600 and 817 cm^{-1} [23, 35-36, 54]. The Valentina and Gucci samples show characteristic bands around 815 cm^{-1}, which may be linked with aromatic isocyanates [7] (Figure 9a-b). This type of TPU is known to be very sensitive to high humidity conditions and prone to partial hydrolysis [7, 27]. Unfortunately, ATR-FTIR did not provide additional information on the polyurethane coating process. As shown in other research, chromatography techniques such as pyrolysis gas chromatography mass spectrometry (Py-GC/MS) or evolved gas analysis (EGA-MS) have proven more accurate in characterizing the products used in its elaboration, the organic additives present, or even the polymer building blocks [7]. These techniques have successfully identified isocyanates used in the production of polyurethane coatings, as well as chain extenders (neopentyl glycol) and additives [7, 27]. The introduction of chain extenders and isocyanates can significantly affect the tensile properties of polyurethanes and their aging process, but further research is needed to understand the role of each chemical component in the degradation of TPUs.

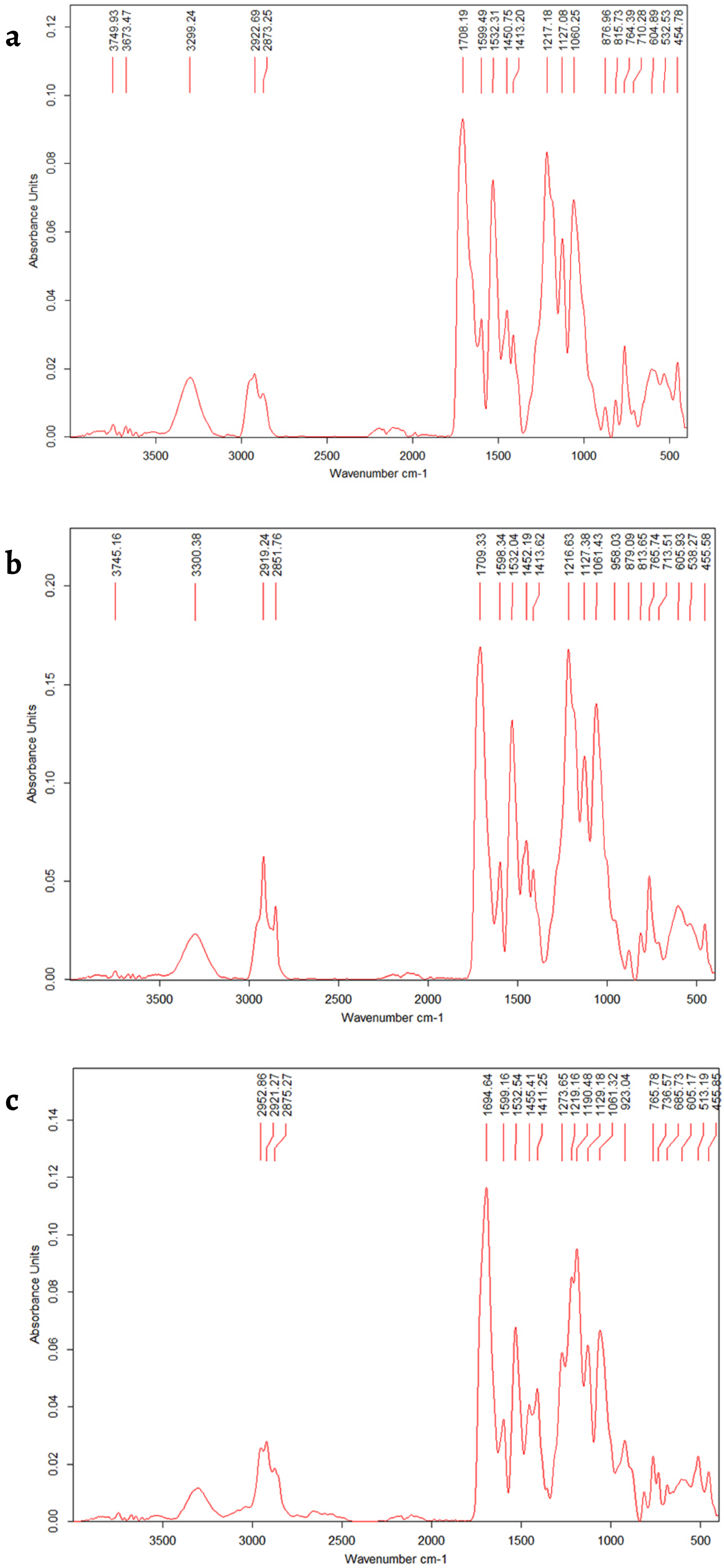

Figure 9. FTIR spectra from: *a)* Valentina boots; *b-c)* Gucci and Charles Jourdan shoes, confirming the presence of polyurethane (TPU) by the characteristic bands around 3300 and 1700 cm^{-1}. The presence of adipic acid is confirmed at the Charles Jourdan (923 cm^{-1}) and TPU aromatic due the wavelengths around 815 cm^{-1}.

Conclusions

The identification of the coating has confirmed the presence of TPU as the main polymer in all three study objects, ruling out any leather dressings. This is particularly important for conservation purposes since the removal of white blooming on traditional leather dressings is typically accomplished with aromatic solvents (such as White Spirit) or alcohol-based solvents. However, their application on TPU surfaces must be approached with caution, as these solvents could dissolve the adipic acid but also damage the TPU. Methanol and ethanol, for instance, have been found to be very effective in removing adipic acid due to their dissolving properties (adipic acid dissolves at 0.0326, and alcohol solvents have effective values around 0.042). In contrast, aggressive solvents such as White Spirit, which perform well with leather dressings, can drastically damage TPU surfaces.

All three shoes exhibited a combination of TPU coatings and leather substrates. The conservation issue identified at the beginning of the research as blooming has proven to be a result of the hydrolysis of ester-aromatic types of TPU, rather than leather dressings. This was particularly confirmed in the Charles Jourdan shoes, where the presence of adipic acid was identified. These findings align with previous research on objects dating to the 1960s and 1970s in other museum collections [26].

Among the shoes tested, all showed the presence of leather substrates, except for the silver edge of the Charles Jourdan shoes, which was finished with a non-woven technology substrate. The results provided additional information about leather processing, identifying the chrome tanning process in the Charles Jourdan shoes as well as the use of grain and corium substrates. According to the literature, chrome offers a very good bond with TPU coatings, especially without the use of any adhesive [24]. Among the three objects, the Valentina boots demonstrated a different approach to leather use, showing corium (sample a) for the most flexible area and grain (sample b) for the most rigid one. This was also confirmed in the other two objects, where grain was identified as the main substrate.

Given the close similarities in production methods, the price differences among the shoes seem to be based on product exclusivity rather than quality. However, to reinforce this assumption, it would be advisable to conduct further analysis using chromatography techniques. Such analyses could help compare the shoes from this research with other existing data, potentially revealing the complexity and technology used in each and providing a more detailed understanding of their production differences. Unfortunately, the field of conservation has not yet reached this stage. While some studies have identified components present in TPU polymers, they have not yet concluded the implications of these differences in terms of production and degradation.

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CONSERVAR PATRIMÓNIO

Synthetic-coated fabrics: challenges and conservation strategies
Tecidos revestidos por filmes sintéticos: desafios e estratégias de conservação
NOTE / NOTA

What smell can tell: using Magic Chemisorbers and GC/MS to capture and analyse volatiles off-gassing from plastic coatings

O que o odor pode dizer: utilização de *Magic Chemisorbers* e GC/MS para capturar e analisar os gases voláteis libertados pelos revestimentos plásticos

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Abstract

Odour that may be released when opening packaging of plastic objects is often a concern for collection managers. Volatile compounds emitted by three separate plastic-coated textile objects from Centraal Museum Utrecht were identified. Samples are analysed with Fourier Transform Infrared Spectroscopy (FTIR) and (pyrolysis) Gas Chromatography Mass Spectrometry (GC/MS). Polar and apolar Magic Chemisorbers are used to trap volatile organic compounds (VOCs) that the plastic coatings are off-gassing. Two of the objects have a plasticised polyvinylchloride (PVC-P) coating giving off a faint chemically sweet smell, where the DEHP plasticiser is detected as the main off-gassing compound. The third object has a polyurethane (PUR) ester coating which has a very rancid smell, most likely a result of the off-gassing of butanoic acid and naphthalene derivatives. This pilot study shows that polar (PEG) and apolar (PDMS) Magic Chemisorbers are useful sorbents to trap compounds that are off-gassing from plastic coatings.

KEYWORDS
Smell
Volatile organic compounds (VOCs)
Plastic coatings
Magic Chemisorbers
Off-gassing

Resumo

Muitas vezes, o odor libertado durante a abertura de embalagens com objetos de plástico é uma preocupação para os gestores de coleções. Foram identificados compostos voláteis emitidos por três objetos têxteis com revestimentos plásticos do Centraal Museum Utrecht. As amostras foram analisadas por FTIR e (py-) GC/MS. *Magic Chemisorbers*, quimiossorventes polares e apolares, foram utilizados para capturar os compostos orgânicos voláteis (VOCs) libertados pelos revestimentos. Dois dos objetos têm um revestimento de poli(cloreto de vinilo) plastificado (PVC-P) que liberta um odor ligeiramente adocicado e o plastificante DEHP foi detetado como o principal composto gasoso a ser libertado. O terceiro objeto tem um revestimento de poliuretano (PUR) à base de éster e liberta um odor rançoso, provavelmente resultante da libertação de ácido butanóico e derivados de naftaleno. Este estudo piloto mostra que os quimiossorventes *Magic Chemisorbers* polares (PEG) e apolares (PDMS) são sorventes úteis para capturar os compostos gasosos libertados por estes revestimentos plásticos.

PALAVRAS-CHAVE
Odor
Compostos orgânicos voláteis (VOCs)
Revestimentos plásticos
Magic Chemisorbers
Libertação de gases

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ARP · Associação Profissional de Conservadores-Restauradores de Portugal · *https://conservarpatrimonio.pt*

Introduction

The odour that may be released when opening packaging of plastic objects is a concern for collection managers. What is that smell? Does the smell say something about the type of plastic, its condition, the possible effect on materials in the immediate environment or the effect on people working in the museum? There is a growing number of plastic objects in museum collections, subsequently the notion that certain plastics can off-gas particular smells increases. This results in more inquiries at the Cultural Heritage Agency of the Netherlands (RCE) about the nature of smell released from plastics.

Throughout *Project Plastics* a collection survey was carried out in 2019 at the Centraal Museum Utrecht, one of the partners in the project. During the survey days, fashion objects ranging from shoes, hats, dresses, accessories, including plastic-coated textiles releasing strong odours were examined. The odorous objects partly inspired the idea for the *Smelly Plastics* project, as follow-up on *Project Plastics* [1-3]. Project *Smelly Plastics* aims to develop a method for sampling and analysis of a wide range of volatile organic compounds (VOCs) off-gassing from plastic museum objects.

When a plastic degrades, the polymer chain is oxidised or hydrolysed and disintegrates into small, often polar, molecules. It is to be expected that degrading plastics will emit acids, aldehydes, ketones, and alcohols [4]. The assumption is made that additives to a plastic, like plasticisers, antioxidants, and/or UV-stabilisers, can evaporate together with volatiles originating from the degradation of the plastic. The smell of a plastic is defined as a mixture of volatile and less volatile, polar and apolar compounds.

For the analysis and identification of volatiles in air, Gas Chromatography Mass Spectrometry (GC/MS) is the method of choice [4-7]. In contrast to previous studies regarding the off-gassing of VOCs from plastics, the starting point of this study is the concern of museum employees about the smell of plastic objects. Research has been conducted into the source and cause of these odours.

Materials and methods

The focus of project *Smelly Plastics* is on plastic artworks and objects present in modern and contemporary art collections. For this research the smell of three plastic-coated textiles from the collection of Centraal Museum Utrecht have been examined (Figure 1).

Figure 1. Three modern, plastic-coated textiles from the collection of Centraal Museum Utrecht: *a)* Girl's raincoat (1972) by Pennel et Flipo; *b)* Children's raincoat (1974) by Barbara Farber; *c)* Woman's ensemble *L'apparence du Vide* (1995) by Viktor & Rolf.

Of the investigated garments the first two are raincoats: a girl's raincoat with a cherry design from Pennel et Flipo dating from 1972 (Figure 1a) and a green children's raincoat from Barbara Farber dating from 1974 (Figure 1b). Both coats have a plastic coating which makes them water repellent. They are stored on a clothes hanger protected with tissue paper.

The third garment is a gold-coloured woman's ensemble named *L'apparence du vide* (1995) by the Dutch fashion house Viktor & Rolf (Figure 1c). It is one of the five garments from Viktor & Rolfs Spring/Summer 1996 collection, which was first shown at a contemporary art gallery in Paris in October 1995. They were presented in the form of an installation, without the use of any models, titled *The appearance of emptiness*. Golden dresses were suspended in the gallery space. On the floor lay black garments made of organza, like shadows. The names of supermodels were written across one wall, while voices on the soundtrack playing in the gallery whispered the names of these supermodels. The supermodel boom had become something of a social phenomenon at the time, causing a huge rise in the fees paid to such models [8]. More attention was often paid to the supermodels themselves than to the designer's collection. Viktor & Rolf were irritated by this situation so they devised a plan to restore the rights of clothes in fashion. Although the golden dresses are three-dimensional, there are no heads or limbs, they are clothes with a shiny surface but no substance, and suspended in the air, they symbolize the emptiness of the fashion world that was in a frenzy over supermodels. The suit is wrapped in acid free tissue paper and stored in an acid free box.

Both sides of the fabric of the three garments were examined. Samples taken were analysed by Fourier Transform Infrared Spectroscopy (FTIR) and pyrolysis Gas Chromatography Mass Spectrometry (py-GC/MS) to determine the material composition of the garments.

FTIR spectral data are collected on a Perkin Elmer Spectrum 100 FTIR spectrometer combined with a Specac Golden Gate Single Reflection Diamond ATR. Taken samples of both sides of the fabric were scanned with 16 scans from 4000 to 450 cm^{-1}. Obtained spectra were compared to a compiled library with plastic reference spectra.

The GC/MS instrument available for both material identification and analysing volatiles emitted by plastics (VOCs) is a Thermo Scientific GC/ISQ-7000 mass spectrometer combination equipped with the Frontier Laboratories 3030D Pyrolyzer and the MicroJet Cryo-Trap 1030Ex. The pyrolyzer is septum-less connected to the GC-column. A split exit is constructed at the base of the pyrolyzer, the carrier and split flows are regulated by the GC [9].

The Frontier Pyrolyzer is used for the material identification of the plastic coating by pyrolysis GC/MS (py-GC/MS), for the analysis of volatiles emitted by the plastics, with material thermal desorption (TD-GC/MS), and for the desorption of VOCs trapped on the Magic Chemisorbers.

For the material identification, type of column and GC/MS settings used are according [9]. The pyrolyzer temperature, for this research, was set at 550 °C.

To analyse VOCs in air, passive sampling with solid phase extraction (SPE) and GC/MS identification were chosen, with the advantage of direct transfer of the captured substances to the inlet of the GC without sample loss due to extraction [10]. With solid phase extraction, VOCs are captured in an activated layer, a sorbent applied on a carrier. The sorbent is subsequently desorbed in the heated inlet of the GC. SPE can be selective and competitive in their sorption of analytes, hence, given the polarity of the expected VOC mixture, it was decided to use both a polar and an apolar coated SPE device.

The capture of VOCs is performed by the recently developed Magic Chemisorber Solid Phase Extraction Elements by Frontier Laboratories Ltd, Japan. They are specially designed for use in their pyrolyzer [11]. Magic Chemisorbers are available in two varieties: polar, de-activated steel coated with polyethylene glycol (PEG matrix) and apolar, titanium coated with polydimethylsiloxane (PDMS matrix). For sampling and analysis of VOCs, the small Magic Chemisorbers are mounted on a (stainless steel) Eco-stick (Figure 2), also necessary to desorb the chemisorbers in the pyrolyzer. The Magic Chemisorbers are cleaned in advance before each sampling by heating them in the pyrolyzer, under an inert atmosphere, for ten minutes at 200 °C (polar chemisorber) and 280 °C (apolar chemisorber). After cleaning, the chemisorbers, mounted on the Eco-stick, are stored in separate sealed vials under an inert atmosphere. To the authors knowledge, this is the first study that uses Magic Chemisorbers in the cultural heritage field to capture the off-gassing compounds released from plastic coatings.

The column used for the analyses of the VOCs is the ZB-5ms (Phenomenex, 7HG-G010-22), an apolar column with a length of 30 m, a diameter of 0.25 mm and a film thickness 1.0 µm. The VOCs obtained are cryo-trapped at -160°C for five minutes at the head of the column prior to analysis. The GC/MS settings used are, helium as carrier gas with a constant flow of 1.4 ml/min, the temperature of the GC inlet is set at 290 °C, the split ratio is set to 1:7. The temperature program used is 80 °C, stable for three minutes, subsequently raised to 200 °C with a rate of 10 °C/min, and to 290 °C with a rate of 6 °C/min, kept stable for three minutes. The temperature of the MS interface is 270 °C, and the temperature of the ion source is set at 250 °C. Mass spectra are recorded from 10 amu until 600 amu with a speed of 5 scans per second.

Direct analysis (TD-GC/MS) of samples of the plastic-coatings was performed, to gain insight about the nature of compounds emitted by the plastics and to verify the results gained with the Magic Chemisorbers. For this, a small sample (app. 10 µg) is placed in a stainless-steel Eco-cup and inserted in the pyrolyzer at 110 °C and kept at that temperature for five minutes. Decomposition of plastics is not expected at 110 °C.

For sampling of the VOCs in air, the object was (partially) covered by a glass bell jar to create a headspace for capturing the compounds emitted by the object. The VOCs are sampled in the immediate vicinity of the artwork, without any direct contact with the SPE devices that are inserted into a piece of polystyrene foam [12]. For analysis of the captured VOCs, the capture elements are thermally desorbed in the heated furnace of the Frontier 3030D pyrolyzer; the polar ones were desorbed at 200 °C, the apolar ones at 280 °C. Desorption time was set to five minutes. Figure 2 depicts the steps in this process. Blank measurements are carried out without the presence of an object under the bell jar and with the presence of the SPE devices in the polystyrene foam mount.

Xcalibur (4.2, Thermo Fisher Scientific) software is used to record the mass spectral data. Amdis 4.71 in combination with a Microsoft Office Excel template is used to identify, sort, and report the results of the analyses [13]. AMDIS (Automated Mass Spectral Deconvolution and Identification System) is a program developed by the National Institute of Standards and Technology (NIST) for the purpose of compound identification in GC/MS [14].

Figure 3 shows the setup in the depot of the Centraal Museum Utrecht for capturing the VOCs emitted by the three garments. Part of the scarf from the Viktor & Rolf women's ensemble is placed under a bell jar together with the Magic Chemisorbers. To prevent the edge of the bell jar from coming into contact with the garment, the garment is covered with tissue paper. To sample the Pennel et Flipo rain jacket, the bell jar was placed directly over one of the sleeves. As there were only two bell jars available, the Barbara Farber children's raincoat was sampled by placing the Magic Chemisorbers in one of the pockets. The time to capture VOCs was set to two hours.

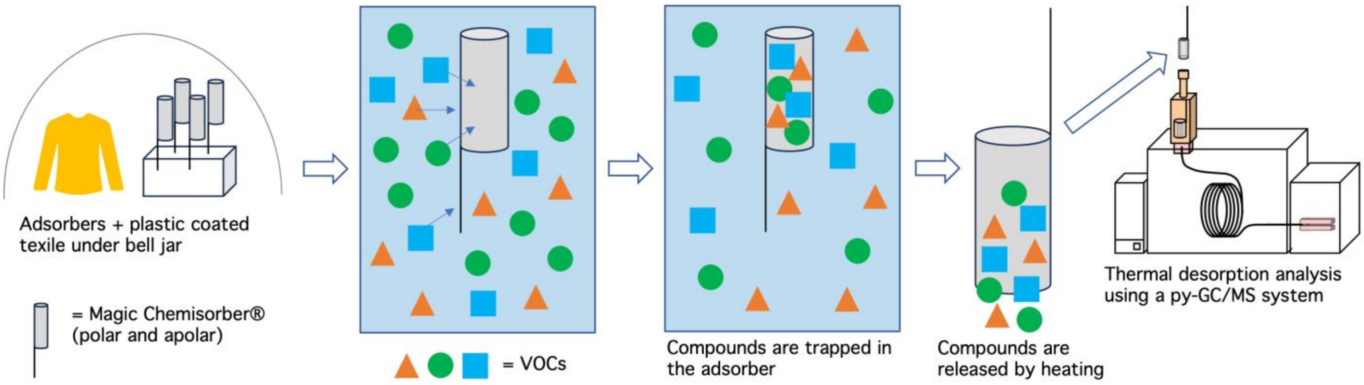

Figure 2. Schematic depiction of the method to capture and analyse VOCs near plastic coated garments.

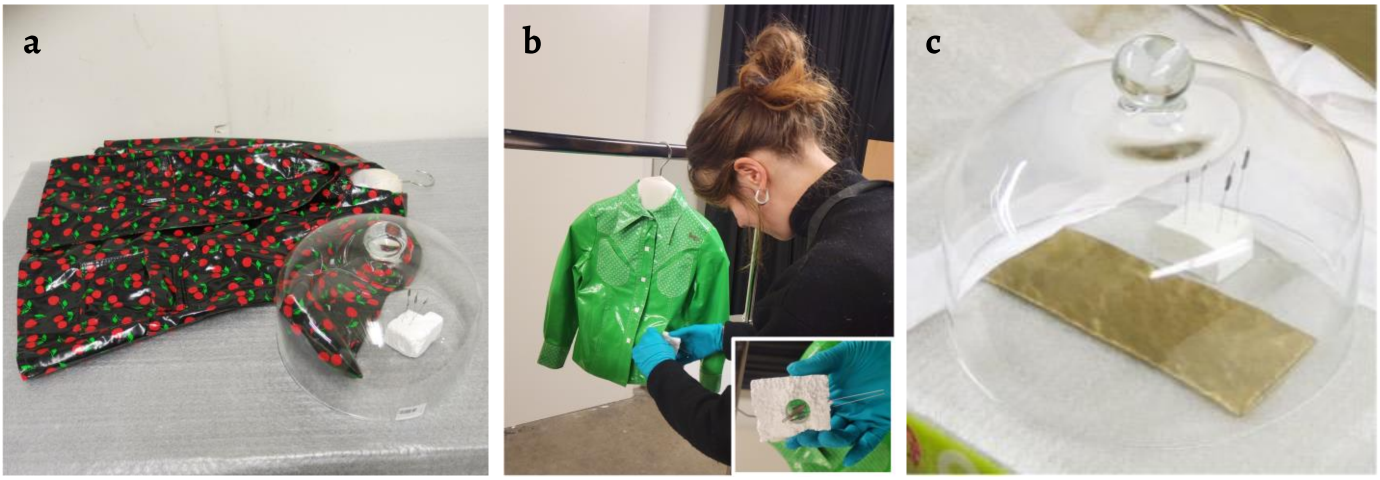

Figure 3. Sampling of the compounds in the air by the Magic Chemisorbers: *a)* Girl's raincoat (1972); *b)* Children's raincoat (1974); *c)* Woman's ensemble *L'apparence du Vide*.

As the project progressed it became clear that more explicit results were achieved if the object was sampled under the bell jar for 72 hours, instead of two hours as used in the first series. This is because the longer sampling time allows more accumulation of evaporating volatiles in the bell jar headspace. It was therefore decided to reanalyse the smelliest garment, *L'apparence du vide* by Viktor & Rolf, with a sampling time of 72 hours.

Results

The obtained results from the analyses of the material samples and captured volatiles are described below. For a clearer representation and interpretation of the volatile compounds emitted by the objects, the results of the polar and apolar chemisorber are presented combined. The analysis of the blank measurements showed that the polystyrene mount did not emit or adsorb VOCs.

Raincoats by Pennel et Flipo, and Barbara Farber

The coats date from the 70s and they both appear in good condition: there are no signs of degradation on the surface and no blooming or weeping is visible. The coats have a slight sweet smell, vaguely reminiscent of cheap inflatables, like swimming rings and beach balls.

FTIR analysis of the material of both raincoats, the girl's raincoat from Pennel et Flipo and the children's raincoat from Barbara Farber, show that the raincoats are very similar in terms of material composition. The presence of bands at 1430 cm^{-1} (CH_2-Cl angular deformation), 1260 cm^{-1} (CH-Cl out of plane angular deformation), 960 cm^{-1} (C-H out of plane trans deformation) and 875 cm^{-1}, 610 cm^{-1} (both C-Cl stretching) allows identification of Polyvinyl Chloride. The addition of a large band at 1724 cm^{-1} (C=O stretching), is due to the presence of plasticiser [15]. Therefore both coatings consist of plasticised Polyvinyl Chloride (PVC-P). In addition, the backing shows a broad band around 3330 cm^{-1} (O-H stretching), 2895 cm^{-1} (C-H stretching), 1029 cm^{-1} (C-O stretching and O-H deformation), and 895 cm^{-1} (linkage between monosaccharides) indicating cellulose (cotton), as stated on each jackets' label [16].

The py-GC/MS analysis of the material of the raincoats shows that the main plasticiser is di(2-ethylhexyl)phthalate (DEHP). This is a widely used plasticiser for PVC-P [17]. In both raincoats plasticisers diisobutyl phthalate (DIBP) and dibutyl phthalate (DBP) are present in trace amounts.

The material thermal desorption analysis (TD-GC/MS) of samples taken from the raincoats, show DEHP plasticiser as main off-gassing compound. Traces of di-isobutyl phthalate (DIBP) and dibutyl phthalate (DBP) were also detected.

The combined results of the polar and apolar Magic Chemisorbers shows the plasticisers DEHP, DIBP and DBP.

L'apparence du vide by Viktor & Rolf

The gold-coloured coating has a very rancid smell and excretes a liquid drenching the tissue paper it is wrapped in. First issues were detected in autumn 2018 after which the collection manager decided to replace the tissue paper. However, during the survey in January 2019, which was only a few months later, the tissue paper had absorbed even more liquid.

The coating (outside) on the Viktor & Rolf garment is characterised with FTIR as a polyurethane ester (PUR ester) due to the presence of the bands at 3294 cm^{-1} (N-H stretching), 1728 cm^{-1} (C=O stretching), 1534 cm^{-1} (N-H deformation), 1231 cm^{-1} and 1173 cm^{-1} (C-N stretching) and 1064 cm^{-1} (C-O-C stretching) [18].The substrate (inside) is characterised as nylon due to the specific amide bands. At 3295 cm^{-1} (N-H stretching), 1635 cm^{-1} (amide I), 1538 cm^{-1} (amide II), and 1261 cm^{-1} (amide III) [19].

Using py-GC/MS, the polyurethane coating is identified as an aromatic PUR ester, consisting of toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI) as the isocyanate building blocks, and polyethylene glycol and polypropylene glycol compounds as the polyol building blocks. Toluenediamine (TDA) and methylene diphenyl diamine (MDA), decomposition products of TDI and MDI, are also detected.

The material thermal desorption analysis (TD-GC/MS) of a sample of the Viktor & Rolf garment shows diethylene glycol, and a compound related to the polyol part of the polyurethane ester, consisting of dimers and trimers of adipic acid and glycol fragments (poly-adipic-glycol compound), as main off-gassing compounds. It also shows the presence of diisopropylnaphthalene-isomers.

The results of the compounds captured by polar and apolar Magic Chemisorbers show diethylene glycol and the poly-adipic-glycol compound as main compounds. Furthermore, butanoic acid and diisopropylnaphthalene-isomers have been captured.

Figure 4 depicts the chromatograms of the material thermal desorption analysis (Figure 4a) and compounds captured by the polar Magic Chemisorber (Figure 4b), the latter is chosen because all main emitted compounds are captured by this type of sorbent. Table 1 presents the results of the main compounds emitted by *L'apparence du vide* using material thermal desorption, and captured with both polar and apolar Magic Chemisorbers.

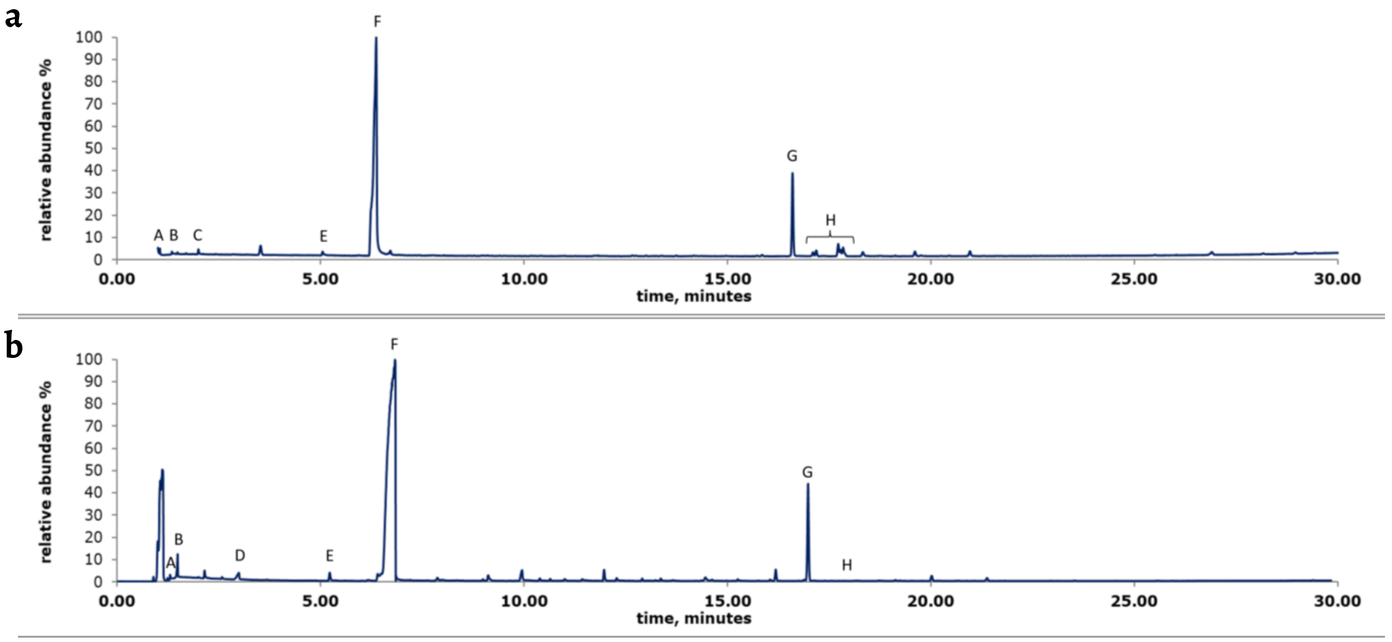

Figure 4. The result of the thermal desorption analysis of: *a)* a small sample of *L'apparence du vide* and *b)* the compounds captured by the polar Magic Chemisorbers after 72h. The main compounds are listed in Table 1.

Table 1. Off-gassed compounds from *L'apparence du vide* identified with thermal desorption and captured with both polar and apolar Magic Chemisorbers.

Label	Compound name	Thermal desorption	Polar & apolar chemisorber
A	Acetone	×	×
B	Acetic acid	×	×
C	Triethyl amine	×	
D	Butanoic acid		×
E	1,4-Dioxan-2-ol	×	×
F	Diethylene glycol	×	×
G	Poly-adipic-glycol component	×	×
H	Diisopropylnaphthalene-isomers	×	×

Discussion and conclusion

The odour of a plastic is always the result of evaporating organic substances, either from additives such as plasticisers and processing aids, or due to the degradation of plastics, where the large polymer molecules break down into smaller volatile compounds. The odour perceived by the human nose is not only dependent on the concentration of different smelly compounds but also on the sensitivity of the human nose. It is possible that a substance, present in very low concentrations, can be easily detected by the human nose, but remains below the detection limit of the method.

Raincoats by Pennel et Flipo, and Barbara Farber

The plastic coating of the raincoats is characterised as PVC-P. Plasticised PVC often expels an odour that can be described as cheap inflatables, like swimming rings and beach balls [1-3]. This smell is noticeable with both raincoats, though, the odour is not that strong. Di(2-ethylhexyl)phthalate (DEHP) is the main plasticiser of the PVC-P coating of the raincoats, together with small amounts of diisobutyl phthalate (DIBP) and dibutyl phthalate (DBP). DEHP has almost no odour, DBP has a slight aromatic odour, and DIBP has a mild odour. This is consistent with the observation that the odour of both raincoats was only slightly perceptible.

The analysis of the captured compounds by the Magic Chemisorbers, with sampling time of two hours, confirms that both raincoats emit the plasticisers DEHP, DIBP and DBP. Both coats appear in good condition: the coating is still flexible. Nevertheless, the plasticisers are evaporating, which indicates that the material will eventually become less flexible and the coating may shrink due to the loss of plasticiser [20]. These are both well-known degradation phenomena for PVC-P [17].

For future research it is interesting to explore the possibility of monitoring the off-gassing of plasticisers, which could help to decide on the most suitable environmental conditions to store these types of garments, thus avoiding the loss of plasticiser.

L'apparence du vide by Viktor & Rolf

The Viktor & Rolf ensemble is coated with an aromatic PUR-ester. The smell of *L'apparence du vide* is rancid, like stale butter. The strong rancid smell of the suit is most likely the result of the off-gassing of butanoic acid and naphthalene derivatives. The origin of these compounds is not clear. According to literature naphthalene derivatives can be used to make monomers of high-performance polyester fibres, moulded plastics and other advanced polymer materials and can exhibit characteristic smells [21-24]. Butanoic acid is known to give off a rancid odour even in low concentrations. It would be interesting to further investigate whether aromatic PUR ester coatings emit these compounds more often.

The main off-gassing compounds, captured by the Magic Chemisorbers, are diethylene glycol and a poly-adipic-glycol component. Both are formed due to degradation by hydrolysis of the soft segment (polyol part) of the PUR ester [25-26].

Magic Chemisorbers

This pilot study shows that polar (PEG) and apolar (PDMS) Magic Chemisorbers are useful sorbents to trap VOCs off-gassing from plastic coatings. Practice has shown that the chemisorbers are robust and can be used several times due to the process of capture and desorption and storage under an atmosphere. An added value for the use of Magic Chemisorbers is that one pyrolysis-GC/MS instrument and set-up is used for all applications (pyrolysis, desorption, and passive sampling), allowing the results to be compared easily and reliably. Ongoing research at the Cultural Heritage Agency of the Netherlands will investigate the long-term efficiency and reusability of the Magic Chemisorbers.

Although a sampling time of two hours is sufficient for the Magic Chemisorbers to capture the volatiles emitted by the sampled object in the bell headspace, this time is too short for emissive volatiles from the objects to equilibrate with the space in the bell jar. It was therefore decided to sample for 72 hours, during which time the object was placed under the bell jar together with the Magic Chemisorbers.

The analytical procedure described can be used to gain insight into which compounds the material off-gasses through non-destructive sampling. This can provide information about the odours that are released, but also about degradation compounds. It is a promising method that should be further investigated and hopefully can be used as a non-invasive technique in the near future.

The safety concerns raised when opening a packaging of a smelly plastic object are justifiable, but also a complex topic and complicated to test. Further research is necessary to be able to provide answers to these questions.

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