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

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].

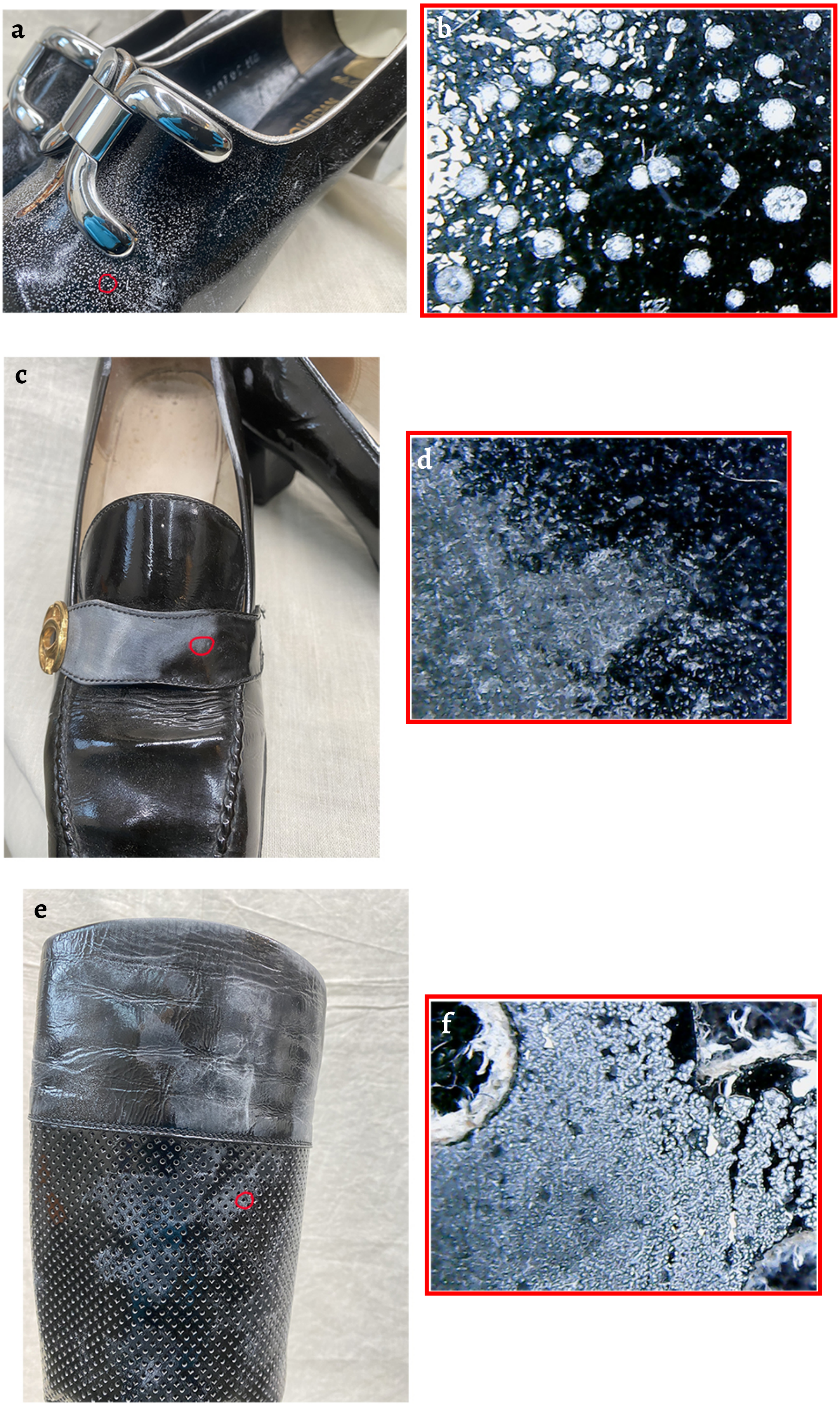

Figure 3. Degradation elements seeing in form of blooming at the three shoes from this research showing a diversity of forms, from a sort of crystals to a cloudy form. Shoes and the details (red) studied with Dino-Lite: *a-b)* Charles Jourdan, *c-d)* Gucci; *e-f)* Valentina.

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.

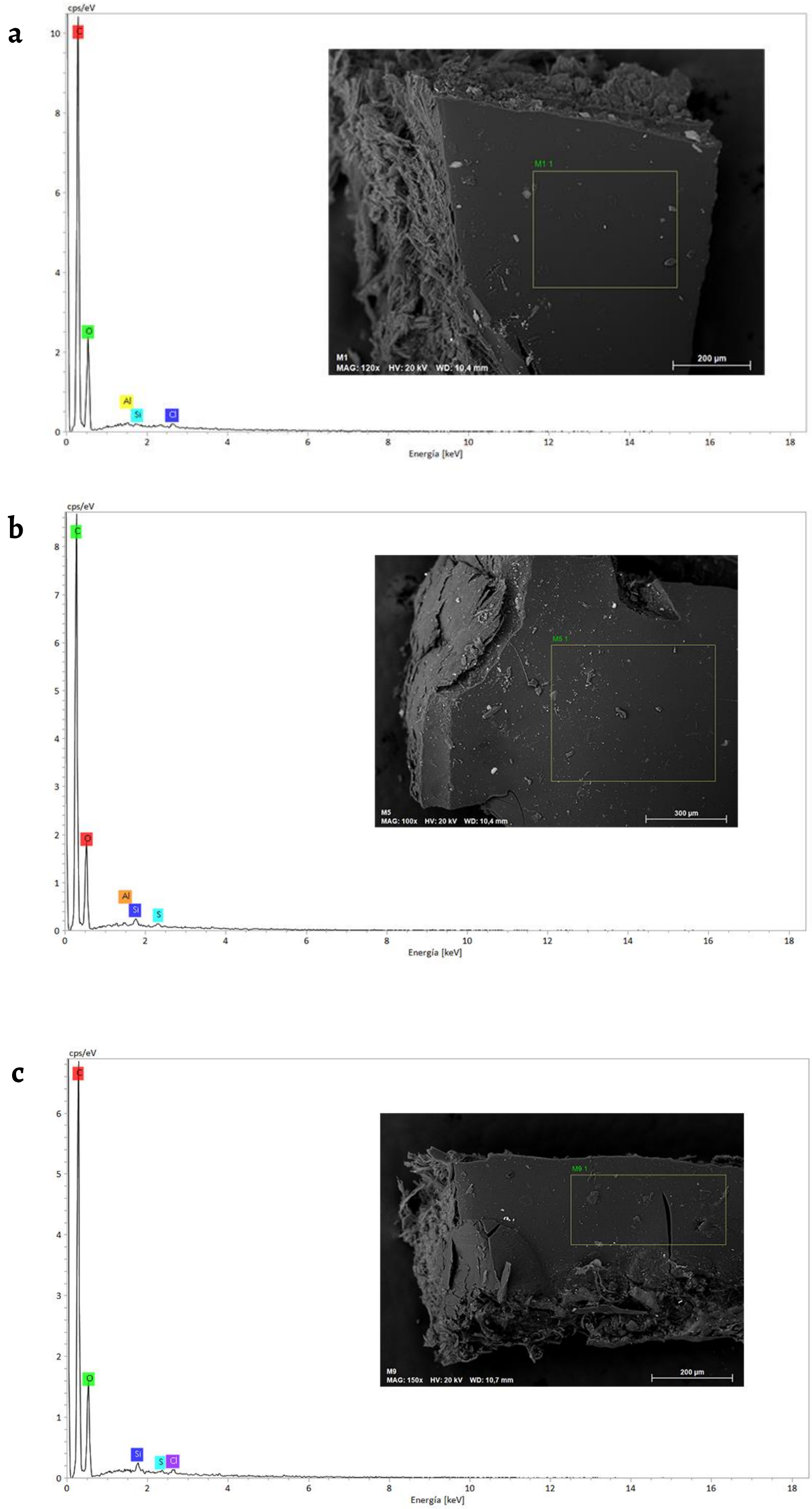

Figure 4. SEM-EDX results carried out over the surface of: *a)* Valentina boots; *b)* Gucci shoes; *c)* Charles Jourdan shoes.

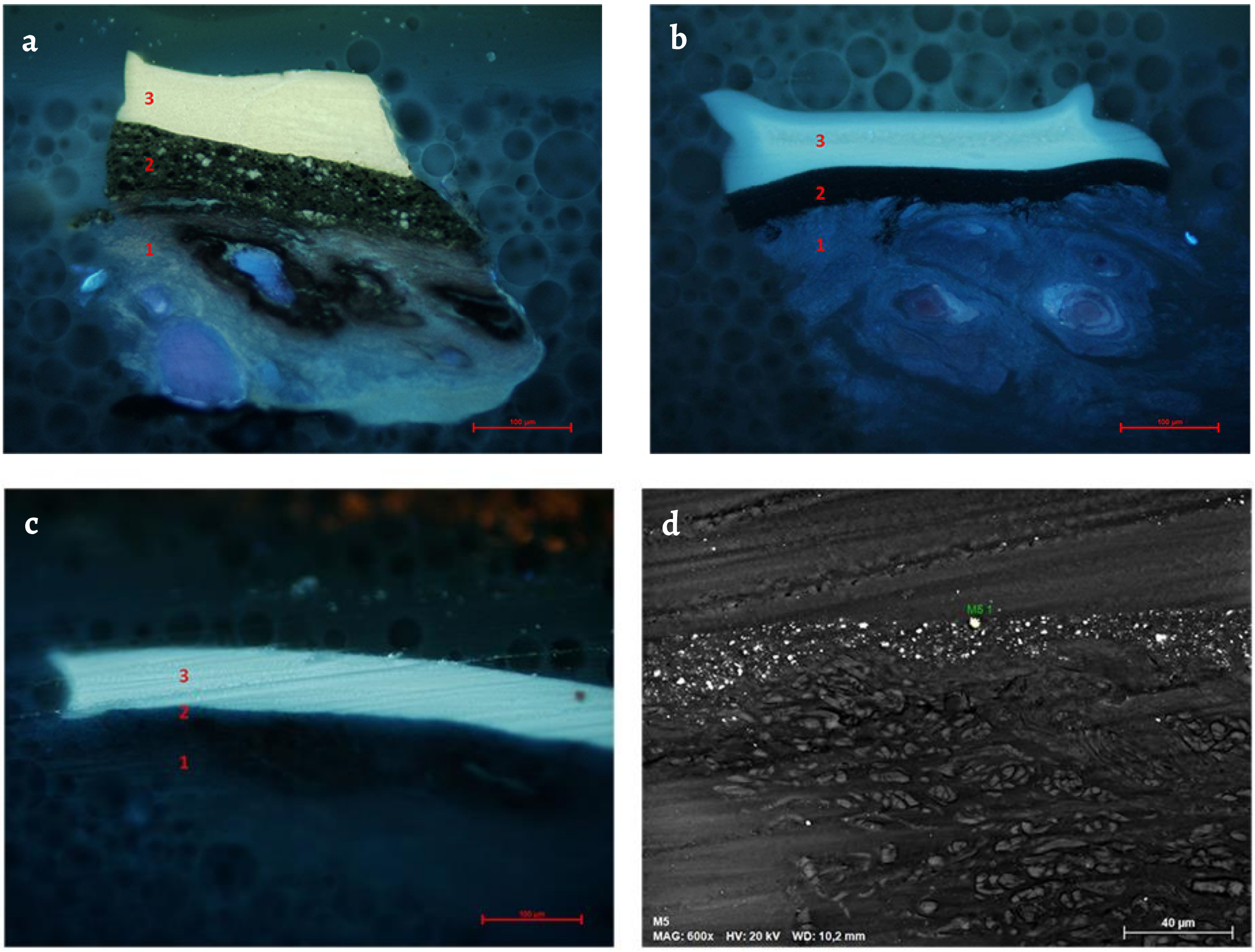

Figure 5. Stratigraphy of the collect samples from: *a)* Charles Jourdan shoe and *b)* Valentina boots, both seen under MO-UV 200×,showing 3 layers in total, differing the interlayer: Charles Jourdan shows a possible presence of a foam layer (2) while the Valentina the characteristic compact layer (2); *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].

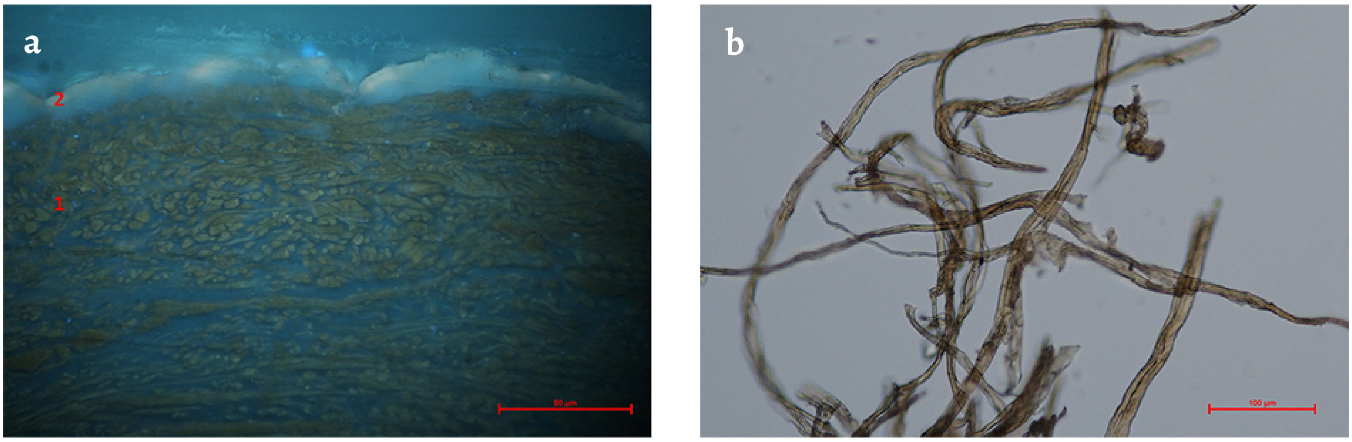

Figure 6. Charles Jourdan shoe: *a)* sample obtained from the silver edge , studied under OM in cross-section in UV mode (unlike the other samples, only two layers are visible; *b)* fibres taken from the substrate showing a slightly twisted core identified as cotton.

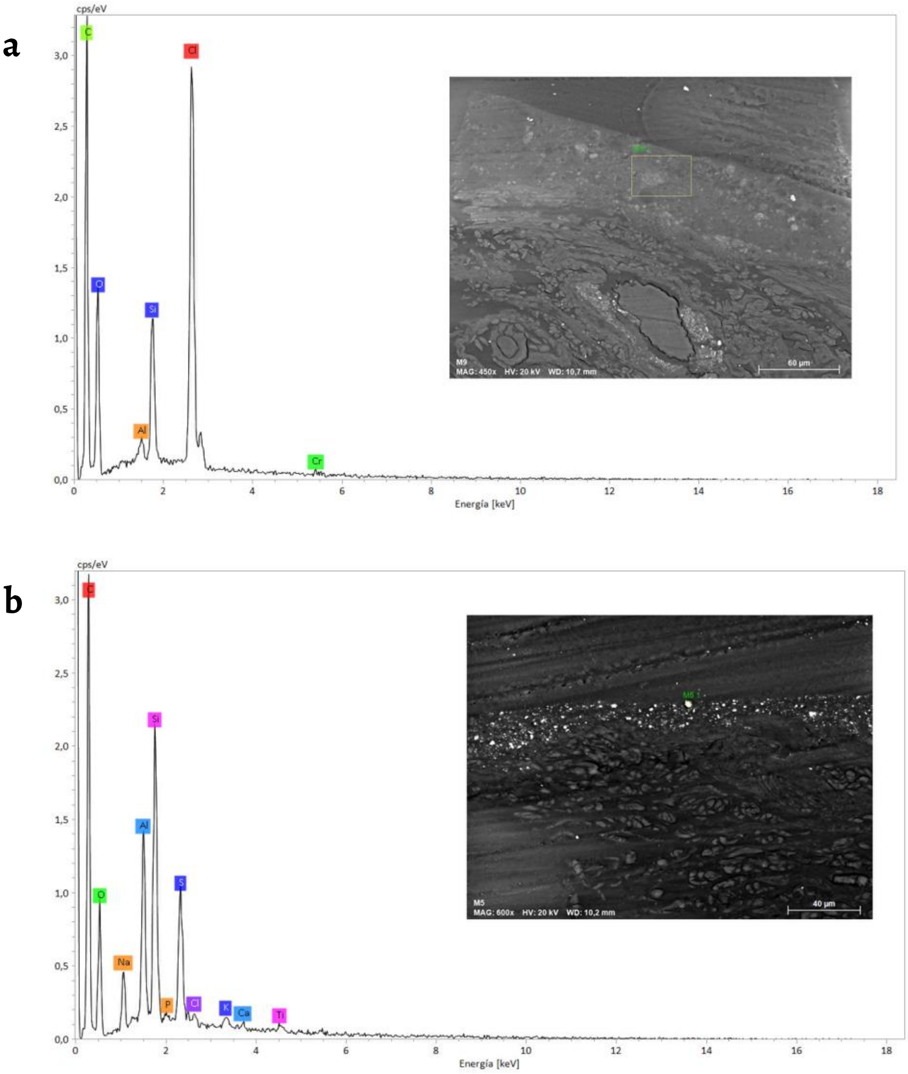

Figure 7. SEM-EDX analysis carried out on the lateral side of the samples: *a)* Charles Jourdan shoes identifying chrome as one of the components on the coating taken from the black sample; *b)* Gucci shoes with the presence of titanium dioxide.

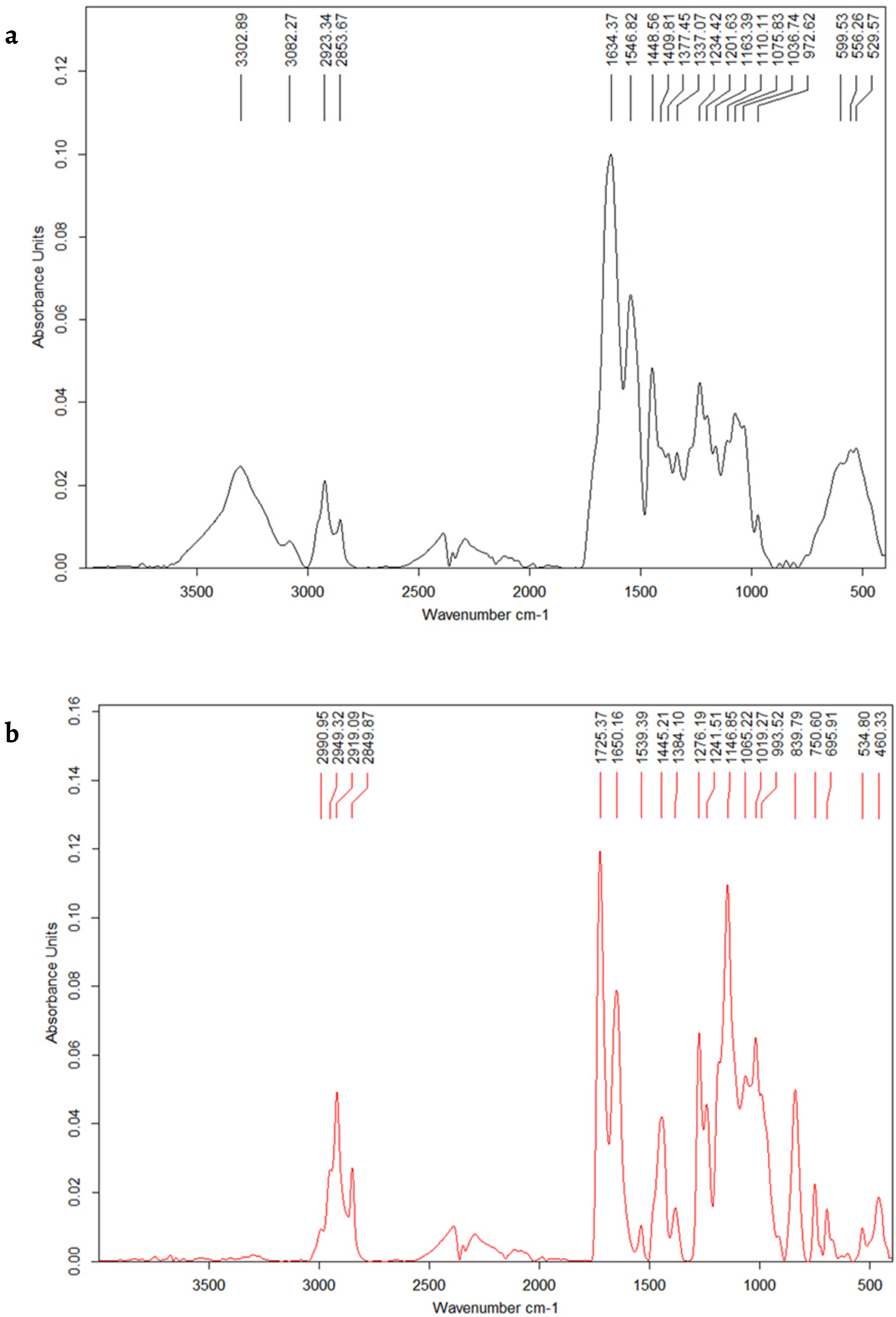

Figure 8. FTIR spectra with the identification of: *a)* nylon by the characteristic wavelengths around 1640 and 3300 cm^{-1}; *b)* the presence of polyacrylic resin by the characteristic bands of 1725, 1445, 1146 and 993 cm^{-1}.

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.

a

b

c

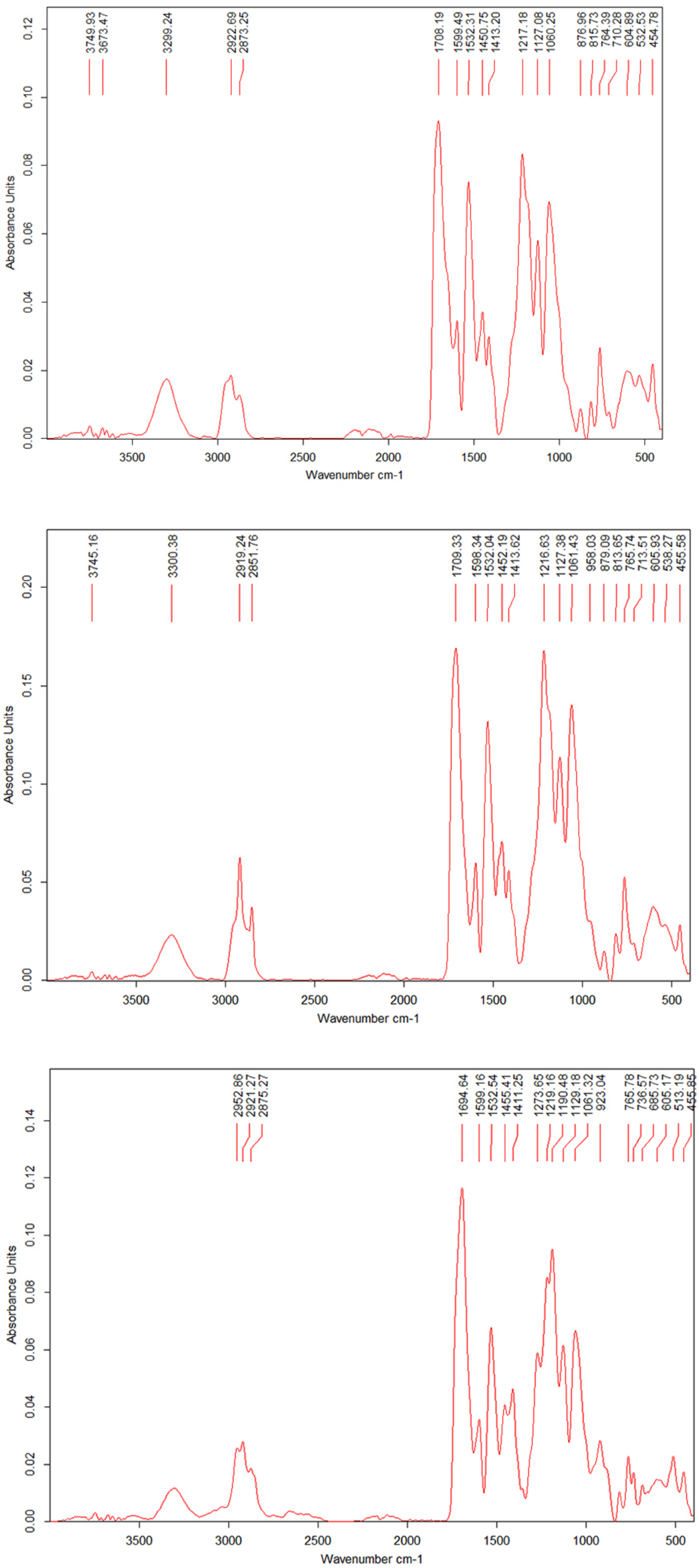

Figure 9. FTIR spectra from: *a)* Valentina boots; *b-c)* Gucci and Charles Jourdan shoes, confirming the presence of polyurethane (TPU) by the characteristic bands around 3300 and 1700 cm^{-1}. The presence of adipic acid is confirmed at the Charles Jourdan (923 cm^{-1}) and TPU aromatic due the wavelengths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