CONSERVAR PATRIMÓNIO
Synthetic-coated fabrics: challenges and conservation strategies
Tecidos revestidos por filmes sintéticos: desafios e estratégias de conservação
in Press **ARTICLE / ARTIGO**

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

ARTUR NEVES [1,2*]
JOANA TOMÁS FERREIRA [2,3]
ROBERT FRIEDEL [4]
MARIA ELVIRA CALLAPEZ [1]

1. Centro Interuniversitário de História das Ciências e da Tecnologia (CIUHCT), Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Lisbon 1749-016, Portugal
2. Department of Conservation and Restoration, NOVA School of Science and Technology, Universidade NOVA de Lisboa, Campus Caparica, Monte de Caparica 2829-516, Portugal
3. LAQV-REQUIMTE, NOVA, Universidade NOVA de Lisboa, 2829-516 Caparica, Portugal
4. Department of History, University of Maryland, 2115 Francis Scott Key Hall, College Park, Maryland 20742, USA

**al.neves@campus.fct.unl.pt*

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].

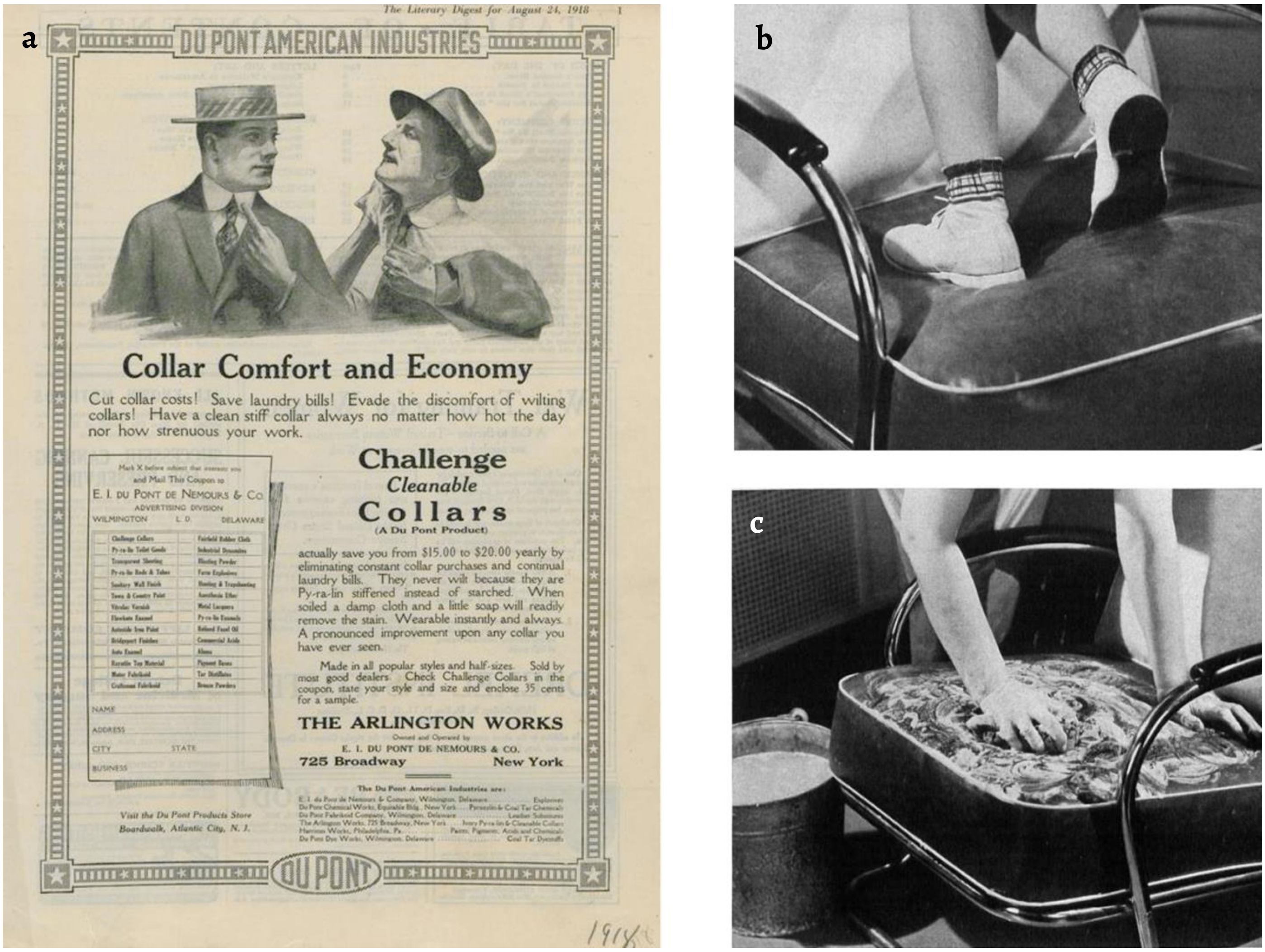
In comparison, this work emphasizes a small list of conservation studies focusing on cellulose nitrate-coated fabrics [16-17]. Ison et al.[16] identified an imitation leather upholstery of a nineteenth-century coach as a cellulose nitrate-coated fabric, stressing that "little is known about the use practices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



The Literary Digest for August 24, 1918

DU PONT AMERICAN INDUSTRIES

Collar Comfort and Economy

Cut collar costs! Save laundry bills! Evade the discomfort of wilting collars! Have a clean stiff collar always no matter how hot the day nor how strenuous your work.

and Mail This Coupon to
E. I. DU PONT DE NEMOURS & CO.
ADVERTISING DIVISION
WILMINGTON L. D. DELAWARE

NAME
ADDRESS
CITY STATE
BUSINESS

Challenge
Cleanable
Collars
(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.

Made in all popular styles and half-sizes. Sold by most good dealers. Check Challenge Collars in the coupon, state your style and size and enclose 35 cents for a sample.

THE ARLINGTON WORKS
Owned and Operated by
E. I. DU PONT DE NEMOURS & CO.
725 Broadway New York

The Du Pont American Industries are:

Visit the Du Pont Products Store
Boardwalk, Atlantic City, N. J.

DU PONT

1918

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.

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.

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 (ν_aNO_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.

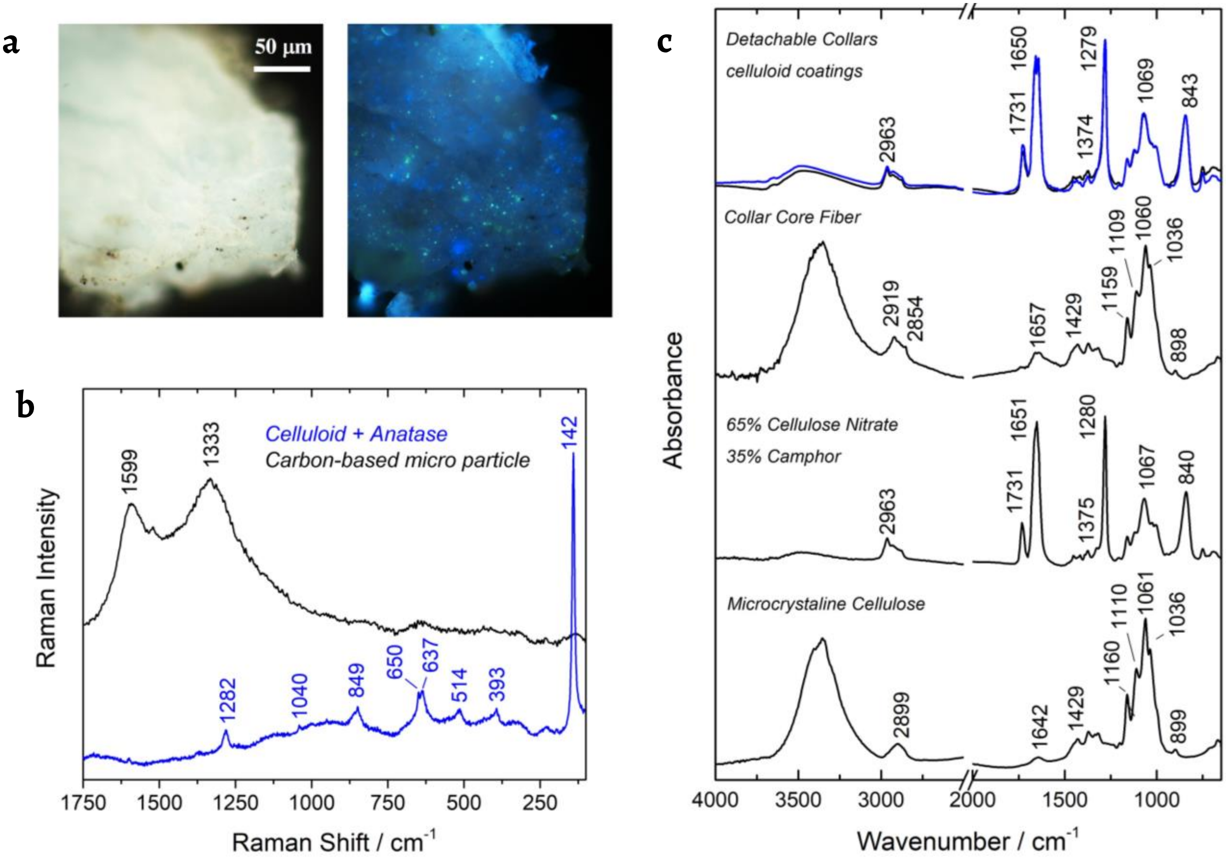


Figure 3. "Collar A": *a-b)* Micrographs (500×) of a microsample observed under cross-polarized light and with UV light (λ_{exc} = 365 nm); *c)* Raman spectra (633 nm laser) of anatase (TiO_2, 120 s acquisition time, 3 cycles) and of a carbon-based particle (60 s acquisition time, 1 cycle); *d)* Infrared 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).

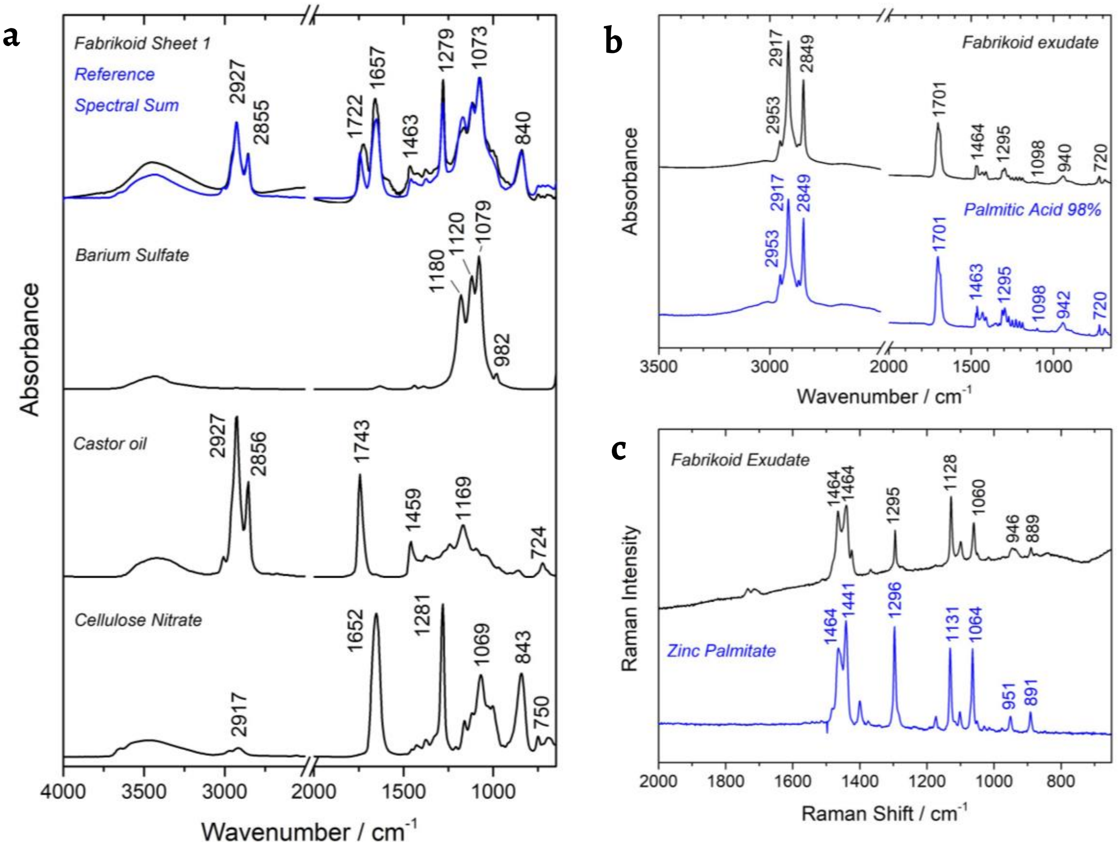


Figure 4. Infrared spectrum of the: *a)* Fabrikoid brochure sheet 1, compared with a spectral sum (proportion 1:1:1) of the reference infrared spectra showed below, namely barium sulfate ($BaSO_4$), castor oil and cellulose nitrate; *b)* Fabrikoid exudate (removed from the Melinex sheet) compared to 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).

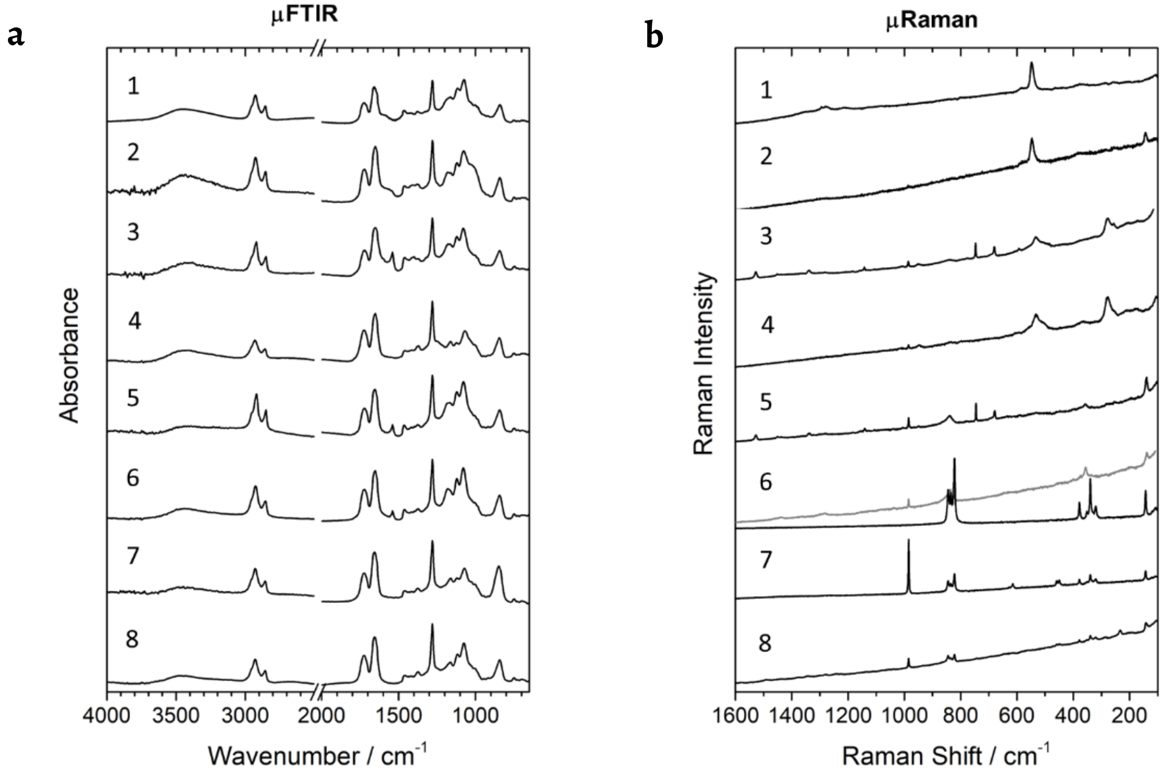
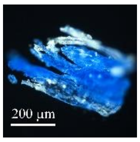
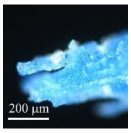
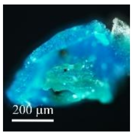
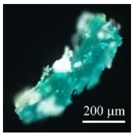
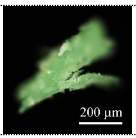
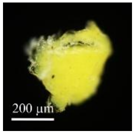
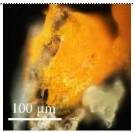
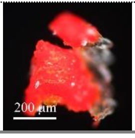


Figure 5. Spectra of the Fabrikoid sheets: *a)* Infrared and *b)* Raman (785 nm laser, 100 mW, 5-50 s acquisition time, 1-5 cycles). For µRaman analysis of sheet 8, a density filter was used (10 mW) due to intense fluorescence background, probably from an organic red pigment.

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).

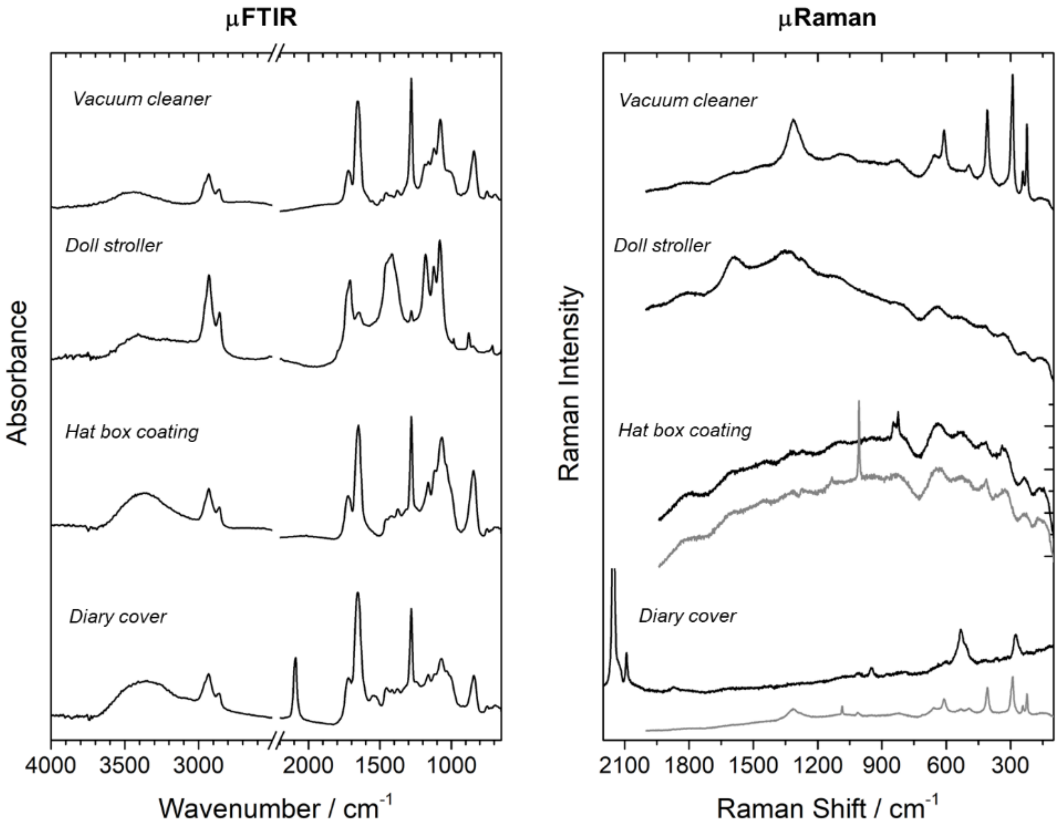


Figure 6. Analysis of the coatings collected from the National Museum of Costumes: *a)* Infrared and *b)* Raman (633 nm laser, 0.17 mW, 30-120s acquisition time, 1-5 cycles) spectra. For the diary cover, an extended spectral window (2200-100 cm^{-1}) was used to observe the C≡N vibrations of Prussian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

Acknowledgements

We thank the Hagley Museum and Library, especially to the conservators Ebenezer Kotei and Laura Wahl, and the National Museum of Costumes (Museu Nacional do Traje), especially to conservator Dina Dimas and collections manager Elsa Ferraz, for selecting the objects and providing all the conditions for micro sampling. This research was supported by Fundação para a Ciência e Tecnologia, Ministério da Educação e da Ciência (FCT/MCTS), Portugal, through the funded project "The Plastics Metamorphoses - the reality and the multiple approaches to a material" (2022.05086.PTDC) and by doctoral grant awarded to Joana Tomás Ferreira (2021.04565.BD). FCT/MCTS and Fulbright Portugal financed this work through a Fulbright research grant awarded to Artur Neves (PS00326022).

REFERENCES

1. Bussiere, P. O.; Gardette, J. L.; Therias, S., 'Photodegradation of celluloid used in museum artifacts', *Polymer Degradation and Stability* **107** (2014) 246-254, https://doi.org/10.1016/j.polymdegradstab.2014.02.022.
2. Berthumeyrie, S.; Collin, S.; Bussiere, P. O.; Therias, S., 'Photooxidation of cellulose nitrate: New insights into degradation mechanisms', *Journal of Hazardous Materials* **272** (2014) 137-147, https://doi.org/10.1016/j.jhazmat.2014.02.039.
3. Shashoua, Y., *Conservation of Plastics: materials science, degradation and preservation*, Elsevier, Oxford (2008).
4. Derrick, M.; Stulik, D., 'Deterioration of Cellulose Nitrate Sculptures Made by Gabo and Pevsner', in *Procedings of a conference symposium – Saving the twentieth century*, ed. D. W. Grattan, Canadian Conservation Institute, Ottawa (1993) 95-102.
5. Paris, C.; Coupry, C., 'Fourier transform Raman spectroscopic study of the first cellulose-based artificial materials in heritage', *Journal of Raman Spectroscopy* **36** (2005) 77-82, https://doi.org/10.1002/jrs.1288.

6. Sutherland, K.; Schwarzinger, C.; Price, B. A., 'The application of pyrolysis gas chromatography mass spectrometry for the identification of degraded early plastics in a sculpture by Naum Gabo', *Journal of Analytical and Applied Pyrolysis* **94** (2012) 202-208, https://doi.org/10.1016/j.jaap.2011.12.016.
7. Lattuati-Derieux, A.; Egasse, C.; Thao-Heu, S.; Balcar, N.; Barabant, G.; Lavédrine, B., 'What do plastics emit? HS-SPME-GC/MS analyses of new standard plastics and plastic objects in museum collections', *Journal of Cultural Heritage* **14** (2013) 238-247, https://doi.org/10.1016/j.culher.2012.06.005.
8. Salvant, J.; Sutherland, K.; Barten, J.; Stringari, C.; Casadio, F.; Walton, M., 'Two Làszló Moholy-Nagy paintings on Trolit: insights into the condition of early cellulose nitrate plastic', *e-Preservation Science* **13** (2016) 15-22.
9. Mazurek, J.; Laganà, A.; Dion, V.; Etyemez, S.; Carta, C.; Schilling, M. R., 'Investigation of cellulose nitrate and cellulose acetate plastics in museum collections using ion chromatography and size exclusion chromatography', *Journal of Cultural Heritage* **35** (2019) 263-270, https://doi.org/10.1016/j.culher.2018.05.011.
10. Neves, A.; Friedel, R.; Melo, M. J.; Callapez, M. E.; Vicenzi, E. P.; Lam, T., 'Best billiard ball in the 19th century: composite materials made of celluloid and bone as substitutes for ivory', *PNAS Nexus* **2** (2023) 1-11, https://doi.org/10.1093/pnasnexus/pgad360.
11. Elsässer, C.; Micheluz, A.; Pamplona, M.; Kavda, S.; Montag, P., 'Selection of thermal, spectroscopic, spectrometric, and chromatographic methods for characterizing historical celluloid', *Journal of Applied Polymer Science* **138** (2021) e50477, https://doi.org/10.1002/app.50477.
12. Neves, A.; Friedel, R.; Callapez, M. E.; Swank, S. D., 'Safeguarding our dentistry heritage: a study of the history and conservation of nineteenth–twentieth century dentures', *Heritage Science* **11** (2023) 142, https://doi.org/10.1186/s40494-023-00989-2.
13. Selwitz, C., *Cellulose nitrate in conservation*, J. Paul Getty Trust, Los Angeles (1988).
14. Allen, N. S.; Edge, M.; Rorie, C. V.; Jewitt, T. S.; Appleyard, J. H., 'The degradation and stabilization of historic cellulose acetate/nitrate base motion-picture film', *The Journal of Photographic Science* **36** (1988) 103-106, https://doi.org/10.1080/00223638.1988.11736978.
15. Shashoua, Y.; Bradley, S. M.; Daniels, V. D., 'Degradation of cellulose nitrate adhesive', *Studies in Conservation* **37** (1992) 113-119, https://doi.org/10.2307/1506403.
16. Ison, N.; Wain, A.; Hoogewerff, J., 'Economy and fashion: analysing the use of simulated leather upholstery in a nineteenth century Australian coach', *Heritage Science* **5** (2017) 9, https://doi.org/10.1186/s40494-017-0122-9.
17. Jastrzębiowska, J.; Wawrzyk, A.; Uroda, N., 'Influence analysis of polyvinyl alcohol on the degradation of artificial leather with cellulose nitrate coating originating from a suitcase stored in the collection of the Auschwitz-Birkenau state museum in Oświęcim, Poland', *Materials* **16** (2023) 7033, https://doi.org/10.3390/ma16217033.
18. Worden, E. C., *The nitrocellulose industry*, vol. II, Constable and Company, London (1911).
19. Friedel, R., *Pioneer plastic: the making and selling of celluloid*, The University of Wisconsin Press, Madison (1983).
20. Meikle, J. L., *American plastic: a cultural history*, Rutgers University Press, New Brunswick (1997).
21. Sanborn, R. H.; Kanouse, C. O.; Sanborn, A. A., *Improvement in collars and cuffs*, U.S Patent 200939 (1878).
22. Ellis, R.T., 'Applying "Pyralin" to Cloth', *The DuPont Magazine* **28** (1934) 16-17.
23. Murphy, M. J., 'Orthopedic manhood: detachable shirt collars and the reconstruction of the white male body in America, ca. 1880–1910', *Dress: The Journal of the Costume Society of America* **32** (2005) 75-95, https://doi.org/10.1179/036121105805253099.
24. Petrov, J., 'Collared: celluloid, masculinity and class', *Critical Studies in Men's Fashion* **3** (2016) 63-78, https://doi.org/10.1386/csmf.3.2.63_1.
25. Laver, M., 'Titanium dioxide whites', in *Artists' pigments a handbook of their history and characteristics*, ed. E. W. FitzHugh, vol. 3, National Gallery of Art, Washington, D. C. (1997) 295-255.
26. Ogunniyi, D. S., 'Castor oil: a vital industrial raw material', *Bioresources Technology* **97** (2006) 1086-1091, https://doi.org/10.1016/j.biortech.2005.03.028.
27. Miles, F. D., *Cellulose nitrate: the physical chemistry of nitrocellulose, its formation and use*, Oliver and Boyd, London (1955).
28. Kanigel, R., *Faux real: genuine leather and 200 years of inspired fakes*, University of Pennsylvania Press, Philadelphia (2010).
29. Wescott, N. P., 'How coated textiles have served', *The DuPont Magazine* **21** (1927) 28-29.
30. Meikle, J. L., 'Presenting a new material: from imitation to innovation with Fabrikoid', *The Journal of the Decorative Arts Society 1850 - the Present* **19** (1995) 8-15, https://www.jstor.org/stable/41805870.
31. Rogers, T. H., *Artificial leather: the degradation of Fabrikoid*, DuPont Fabrikoid Division, Delaware (1922).
32. Quye, A., 'Quality matters for historical plastics: the past-making of cellulose nitrates for future preservation', *Cahiers François Viète* **III** (2017) 45-65, https://doi.org/10.4000/cahierscfv.799.
33. Osmond, G., 'Zinc soaps: an overview of zinc oxide reactivity and consequences of soap formation in oil-based paintings', in *Metal soaps in art – conservation and research*, eds. F. Casadio, K. Keune, P. Noble, A. Van Loon, E. Hendriks, S. A. Centeno, and G. Osmond, Springer, e-book (2019) 25-46, https://doi.org/10.1007/978-3-319-90617-1.
34. Anon.,'C. E. Buckley one of youngest industries operating in the city', *Leominster Daily Enterprise*, Leominster (21st October 1939) 10, https://leominster.advantage-preservation.com/.
35. Otero, V.; Sanches, D.; Montagner, C.; Vilarigues, M.; Carlyle, L.; Lopes, J. A.; Melo, M. J., 'Characterisation of metal carboxylates by Raman and infrared spectroscopy in works of art', *Journal of Raman Spectroscopy* **45** (2014) 1197-1206, https://doi.org/10.1002/jrs.4520.
36. Neves, A.; Angelin, E. M.; Roldão, É.; Melo, M. J., 'New insights into the degradation mechanism of cellulose nitrate in cinematographic films by Raman microscopy', *Journal of Raman Spectroscopy* **50** (2019) 202-212, https://doi.org/10.1002/jrs.5464.

37. Coccato, A.; Jehlicka, J.; Moens, L.; Vandenabeele, P., 'Raman spectroscopy for the investigation of carbon-based black pigments', *Journal of Raman Spectroscopy* **46** (2015) 1003-1015, https://doi.org/10.1002/jrs.4715.
38. Ohsaka, T.; Izumi, F.; Fujiki, Y., 'Raman spectrum of anatase, TiO2', *Journal of Raman Spectroscopy* **7** (1978) 321-324, https://doi.org/10.1002/jrs.1250070606.
39. McHale, J. L.; Knorr, F. J., 'Photoluminescence and carrier transport in nanocrystalline TiO2', in *Handbook of luminescent semiconductor materials*, eds. L. Bergman and J. L. McHale, CRC Press, Boca Raton (2012) 365-389.
40. Derrick, M. R.; Stulik, D.; Landry, J. M., *Infrared spectroscopy in conservation science*, The Getty Conservation Institute, Los Angeles (1999).
41. Van der Weerd, J.; Van Loon, A.; Boon, J. J., 'FTIR studies of the effects of pigments on the aging of oil', *Studies in Conservation* **50** (2005) 3-22, https://doi.org/10.1179/sic.2005.50.1.3.
42. Omori, K., 'Infrared diffraction and the far infrared spectra of anhydrous sulfates', *Mineralogical Journal* **5** (1968) 334-354, https://doi.org/10.2465/minerj1953.5.334.
43. Liu, C.; Wang, D.; Zheng, H., 'In situ Raman spectroscopic study of barite as a pressure gauge using a hydrothermal diamond anvil cell', *Applied Spectroscopy* **70** (2016) 347-354, https://doi.org/10.1177/0003702815620556.
44. Araújo, S. V.; Rocha, B. S.; Luna, F. M. T.; Rola Jr, E. M.; Azevedo, D. C.; Cavalcante Jr, C. L., 'FTIR assessment of the oxidation process of castor oil FAME submitted to PetroOXY and Rancimat methods', *Fuel Processing Technology* **92** (2011) 1152-1155, https://doi.org/10.1016/j.fuproc.2010.12.026.
45. Osticioli, I.; Mendes, N. F. C.; Nevin, A.; Gil, F. P.; Becucci, M.; Castellucci, E., 'Analysis of natural and artificial ultramarine blue pigments using laser induced breakdown and pulsed Raman spectroscopy, statistical analysis and light microscopy', *Spectrochimica Acta Part A* **73** (2009) 525-531, https://doi.org/10.1016/j.saa.2008.11.028.
46. Kulesza, P. J.; Malik, M. A.; Denca, A.; Strojek, J., 'In situ FT-IR/ATR spectroelectrochemistry of Prussian blue in the solid state', *Analytical Chemistry* **68** (1996) 2442-2446, https://doi.org/10.1021/ac950380k.
47. Ospitali, F.; Bersani, D.; Di Lonardo, G.; Lottici, P. P., '«Green earths»: vibrational and elemental characterization of glauconites, celadonites and historical pigments', *Journal of Raman Spectroscopy* **39** (2008) 1066-1073, https://doi.org/10.1002/jrs.1983.
48. Anghelone, M.; Jembrih-Simbürger, D.; Schreiner, M., 'Identification of copper phthalocyanine blue polymorphs in unaged and aged paint systems by means of micro-Raman spectroscopy and Random Forest', *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy* **149** (2015) 419-425, https://doi.org/10.1016/j.saa.2015.04.094.
49. Otero, V.; Pinto, J. V.; Carlyle, L.; Vilarigues, M.; Cotte, M.; Melo, M. J., 'Nineteenth century chrome yellow and chrome deep from Winsor & Newton', *Studies in Conservation* **62** (2016) 123-149, https://doi.org/10.1080/00393630.2015.1131478.
50. Castro, K.; Vandenabeele, P.; Rodríguez-Laso, M. D.; Moens, L.; Madariaga, J. M., 'Micro-Raman analysis of coloured lithographs', in *Analytical and Bioanalytical Chemistry* **379** (2004) 674-683, https://doi.org/10.1007/s00216-004-2642-x.

RECEIVED: 2024.2.28
REVISED: 2023.3.28
ACCEPTED: 2024.6.11
ONLINE: 2024.7.10