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Exploratory investigation of historical decorative laminates by means of vibrational spectroscopic techniques

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Abstract

Literature research revealed that scientific work on the characteristics of historical decorative laminates (DLs), like typology, and particularly the material-technical aspects related to the composition and build-up is scarce in the field of conservation-restoration of modern materials. This paper aims to take the first step towards filling in this knowledge gap by demonstrating that an in-depth literature research and complementary chemical-physical analytical techniques are useful in characterising and contextualising historic decorative laminates. This research focused on gaining additional information within chemical analyses on material-technical insights. This could serve as a basis for a more comprehensive historical context. Several historical samples from different sample-catalogues and museum objects, spanning a period from 1953 to 1993, were collected and their respective cross-sections were characterised with infrared (mapping), FT-Raman, and dispersive micro-Raman spectroscopy. The different layers, such as the protective, decorative, and core layers were investigated, and materials such as melamine formaldehyde, urea formaldehyde, cellulose, lignin, titanium dioxide (rutile), zinc sulphide, synthetic organic pigments PR112 (monoazo pigment, Naphthol AS), and PG8 (azo metal complex, Pigment Green B) were detected.

Keywords Historical decorative laminate, FTIR mapping, Raman, Heritage science, Melamine formaldehyde, Urea formaldehyde, Pigments, Kraft paper

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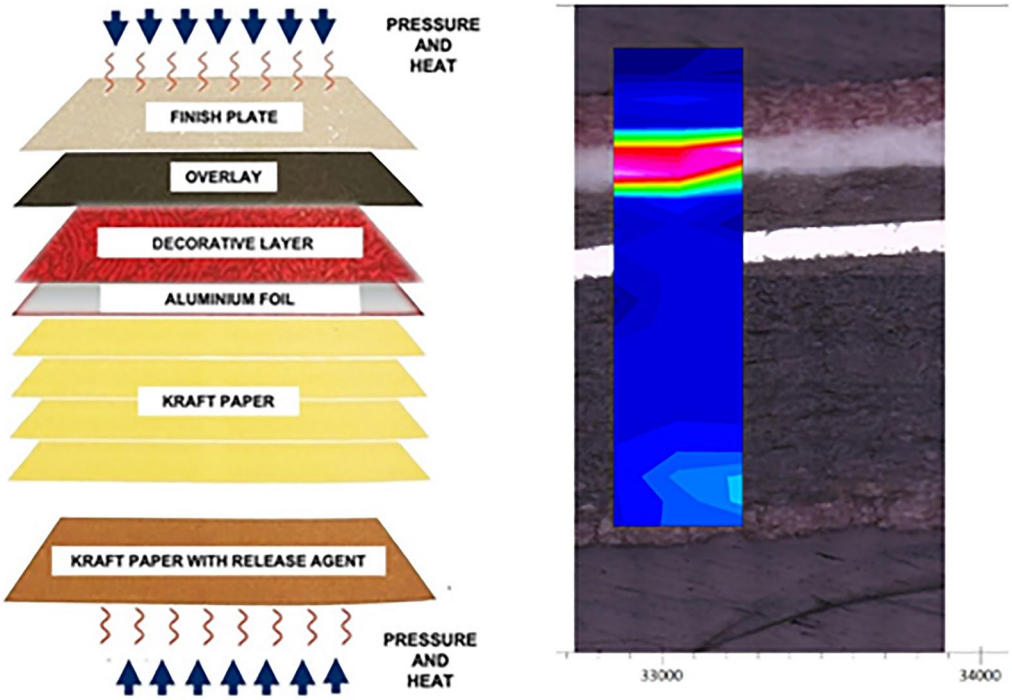
Graphical Abstract



Introduction

Decorative laminates (DLs) are hard and multi-layered finishing materials of the modern times, constructed of sheet material in combination with a thermosetting resin and finished with a monochrome or decorated surface. Due to their relatively low production costs, durability, functional, and decorative versatility, DLs became one of the most widely used materials in interior/exterior decoration of the twentieth century [1].

DLs were used for heavy-duty surfaces like chair-seating, wood-imitation flooring, and kitchen-countertops but also for pure aesthetic reasons like the playful geometric patterns seen on 1980s furniture, for instance, the 'Royal Sofa' by Nathalie Du Pasquier or the 'Carlton Room Divider' by Ettore Sottsass. Literature research shows that since their introduction in the 1930s, a rich variety of production techniques and materials for making DLs have been used [1–3]. Table 1 summarises the build-up of decorative laminates as it was known in 1995. Commonly, the DLs' are built-up (Fig. 1) of single to multiple sheets of paper, impregnated and adhered to one another by a resinous substance (core), which are, after curing, covered by a decorative layer (printed pattern or monochrome) and a protective layer (overlay) with a similar refractive index as the coating resin to retain transparency for the underlying decorative layer.

Table 1 Overview-example of the build-up of decorative laminates (1995, UK), with material, number of layers per type of laminate

Component	Material		Designation or type of laminate	
	Binding medium	Paper type	HGS (horizontal grade standard)	VGS (vertical grade standard)
Overlay	Melamine–formaldehyde	α-cellulose	1	1
Print	Melamine–formaldehyde	Printed pigmented	1	1
Core	Phenol–formaldehyde	Kraft paper	4 to 6	3 to 4

Adapted from [1]

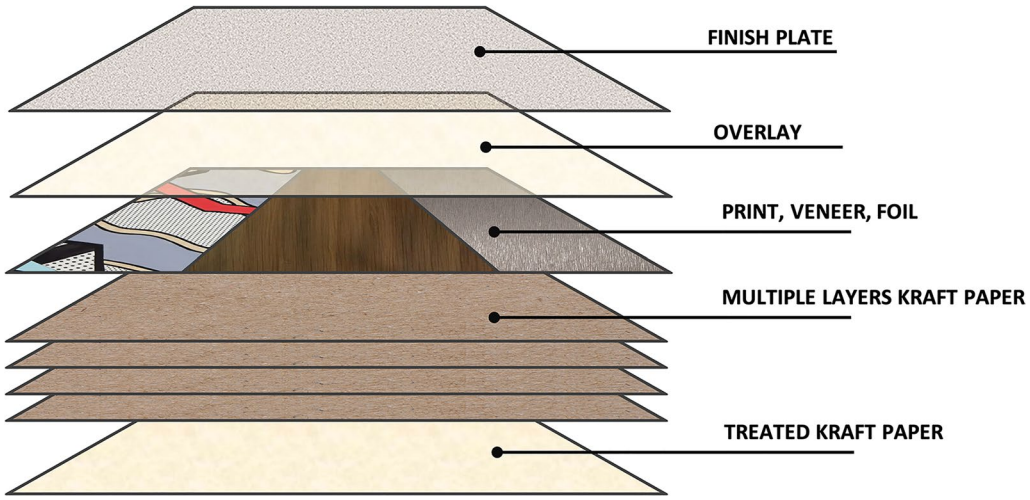


Fig. 1 Decorative laminates' build-up

Phenol formaldehyde was the first commercially available binding medium for making DLs, followed by the lighter coloured urea formaldehyde. Around 1939 melamine–formaldehyde resin was commercialised and used as a resinous impregnating and binding medium for the paper-sheets as well as for the decorative and protective layers. However, for economic reasons, other cheaper synthetic resins such as phenol formaldehyde and urea formaldehyde were also used, in combination or singly, for this purpose [1, 4].

Scientific investigation using multi-analytical methods plays a fundamental role in the field of heritage science [5, 6] as it results in complementary qualitative and/or quantitative information on the composition of the materials allowing for the contextualisation of the historical object. However, acquiring and interpreting the analytical results is challenging due to the inherent instrumental limitations, and sample related limitations such as sample-size and heterogeneity, their representativeness, sampling, sample quality, etc., that always calls for the use of complementary analytical techniques. Raman spectroscopy [7] is an established analytical technique for the identification of a broad range of materials used by artists, such as inorganic [8, 9] and synthetic pigments [10], and other [11] materials and their degradation products [12]. It can be used to examine various objects, including twentieth century objects such as modern paintings [13]. In addition, infrared spectroscopy also offers great potential for the identification of modern materials, such as various synthetic resins used in works of art [13–15]. Moreover, FTIR spectroscopy coupled to microscopic imaging and/or mapping capacity demonstrates a great analytical approach for the investigation of the multilayer structure of cultural heritage (CH) samples which are composed of different organic and inorganic materials, such as binders, pigments, fillers, protective layers, etc [16, 17]. Furthermore, investigation of heterogeneous CH samples can be very efficient when vibrational molecular spectroscopic techniques such as infrared and Raman spectroscopy are complemented.

The research within this IPERION HS (Integrating Platforms for the European Research Infrastructure on Heritage Science) Trans-National Access (TNA) 'Identifying decorative laminates (IDeLA)' project was dedicated to the characterisation of decorative laminates. To do so, infrared (mapping), and FT-Raman and Raman spectroscopy were employed to complement other results obtained by optical microscopy. The main goal was to offer in-depth material technical characterisation of historical decorative laminates (in this study delineated between 1930s and 1993), which have not, based on our knowledge, been studied analytically to such an extent until now.

An additional aim is the use of spectroscopic techniques to differentiate the diverse sample collection of historical DLs on a material level, in order to apply this as a recognition aid. However, for this research only, it was important to carry out an initial identification of the content substances (binder, strengthener, fillers, additives, pigment etc.) and layering.

Methods/experimental

Samples

For this study a total of ten historical decorative laminates samples were selected. The samples were obtained from the historical laminate sample-collection of the Technische Hochschule Köln—Cologne Institute for Conservation Sciences (hereafter, CICS, Fig. 2), twentieth century

Fig. 2 Examples of sample books from the collection in Köln (CICS—Prof. Waentig)

Fig. 3 Sample DL15 was taken from: Desk by Willy Van Der Meeren and Eric Lemesre for Tubax (1954) owned by Design Museum Ghent

Fig. 4 Sample DL16 was taken from Royal chaise longue, for Memphis, 1983, N. Du Pasquier and owned by Design Museum Ghent

Fig. 5 Sample DL24 was taken from the Salon Rose-Marie (LM-173004) property of the Swiss National Museum (image by Hélène Wächter)

objects from the collection of the Design Museum Gent (DMG) (Figs. 3, 4), historical sample books from the archives of the Biennale Interieur Kortrijk (BIK), and a sample from a complete interior 'Salon Rose Marie' from the Schweizerisches Nationalmuseum (Fig. 5).

The selection consisted of a series of samples that were dated between 1950 and 1993, as this period is considered evolutionarily important in the production and usage of decorative laminates. Since the aim of this study is to lay the foundation for future research, the samples were selected according to their diversity, i.e. differences in terms of colour (e.g. white, red, and blue), thickness, design of the decorative paper, and origin of production (Table 2). And finally, to be able to fully understand the results, it was important to know enough background information (like manufacturer, function, and location) about the samples.

The set of samples selected for chemicophysical analysis with FTIR, FT-Raman and Raman spectroscopy is presented in Table 2, where information on the year, brand/producer, general characteristics, or specific details like designer of the object, thickness, original name, and the owner are also included.

Sample preparation for analysis

There are some points to keep in mind when preparing the samples. First, the hardness of decorative laminates causes difficulties in getting good intact and small samples. Second, for optimal study of the samples, it is desired that the sample surface is as smooth as possible; lowering the depth of field for optical microscopy increases the readability of the sequence and morphology of the layers. However, during the process of polishing, cross-contamination of the resin matrix over the surface must be avoided, which might inhibit or influence the quality of the analysis itself. This can be done by cleaning the samples.

Table 2 Description of the samples

Sample n°	Label	Year	Brand/ Producer	Characteristics	Thickness (mm)	Original name	Owner
1	DL06	1966	FORMICA	1 sided—Red	1.4	V88	TH Köln – CICS
2	DL09	1970	RESOPAL	Gloss surface—cream colour	1.2		TH Köln – CICS
4	DL12	1953	Römmler (Resopal)	2 sides—Red (the oldest sample)	1.2	Plastic school: phenoplaste, aminoplaste	TH Köln – CICS
5	DL15	1958	Römmler (Resopal)	Desk by Willy Vandermeeren	1.4	DMG_T_00080_2-2_ ORANJE	Design museum ghent
6	DL16	1983	ABET LAMINATI	Chaise longue by nathalie du pasquier	0.9	1990–0057	Design museum ghent
7	DL18	1993	ABET LAMINATI	Similar print as DL16	0.9	decor Serigrafia 507	Biënnale interieur (Kortrijk)
8	DL20	1993	ABET LAMINATI	Glow-in-the-dark	1.35	Lumiphos 741	Biënnale interieur (Kortrijk)
9	DL22	1993	ABET LAMINATI	Core and decor in red: exterior use	1.25	Colorpact 431	Biënnale interieur (Kortrijk)
10	DL24	1959	FORMICA	Blue		Salon rose-marie sample P6	Schweizerisches nationalmuseum

In this study for optical microscopy and FT-Raman spectroscopy, bare samples (i.e. not embedded in a resinous matrix) were used for the analysis. The surface of these samples was smoothed by cutting the surface with a sharp knife of a sledge-microtome. In relation to optical microscopy, and due to the experimental nature of the research, it was also an aim to find a suitable preparation method that would provide detailed, clear visual images. Although the optical microscopy images presented were obtained on non-embedded samples, the quality of the optical microscopy images could be improved on the cross-section of resin-embedded samples. However, the presented optical images did not hinder the quality of Raman and FTIR analysis.

For the preparation of cross-sections of samples for FTIR mapping and dispersive Raman spectroscopy, the samples were embedded in a two-component resin Kristal PS (Samson Kamnik d.o.o.), containing styrene. Then, they were ground and polished until the cross-section or stratigraphy of all the layers was present on the surface of the embedding resin. A RotoPol-15 sanding and polishing device, silicon carbide sanding papers of various granulations (180–4000), and paraffin oil were used for sanding and polishing. Sanded and polished samples were then cleaned in petroleum ether in an ultrasonic bath (Sonis 2, Iskra Pio).

Optical microscopy

All samples were examined and documented by optical microscopy using bright field and polarised light and under different magnifications. For the samples DL06, DL09, DL12, DL15, DL16, DL18, DL20, DL22, micrographs were acquired with a 3D digital microscope (Olympus DSX510-HRSU). Sample DL24 was recorded with an Axioplan Microscope Zeiss (Kamera Axiocam 305 color, Software ZEN 3.0 Carl Zeiss).

FTIR spectroscopy

FT–IR analysis was performed on a Hyperion 3000 FT–IR microscope coupled with a Tensor spectrometer (Bruker Optics, Inc.) with a liquid nitrogen cooled MCT (mapping measurements) detector. The microscope is combined with 20× micro-ATR objective (germanium hemisphere crystal), which is suitable for mapping/imaging the cross-sections of the samples. The infrared spectra in the range of 4000–650 cm^{-1} were acquired with 64 scans at a resolution of 4 cm^{-1}. The system was operated by the proprietary 32-bit software OPUS 8.1 (Bruker Optik GmbH) during measurements and analyses.

Dispersive Raman spectroscopy (microscopy)

Raman analysis of the cross-sections of the samples was performed using a 785 nm laser excitation line with a Bruker's SENTERA II dispersive Raman micro-spectrometer. The spectra were recorded using a 20× objective lens and a 400 grooves/mm grating, which gave a spectral resolution of approx. 4 cm^{-1}. A multi-channel, TE (thermo-electrically) cooled CCD detector was used. Experimental parameters were adjusted for each sample. Typically, a power of 25 mW (25%, output laser power) was used, and integration times between 20 and 50 s with 2 accumulations.

FT-Raman spectroscopy

FT-Raman spectra were obtained on bare (raw) samples (top and bottom layer) with a Bruker MultiRAM

spectrometer. Nd: YAG laser wavelength of 1064 nm was used for excitation. The resolution was set to 4 cm^{-1} and a 180° geometry was employed. The output laser power and the number of scans were adjusted for each sample. Power between 50 and 500 mW was used, with the number of scans between 256 and 500.

For interpretation of the Raman and FT-Raman spectra, different literature, in-house spectral database or the spectral library available on the internet [10, 18, 19] were used.

Results and discussion

The samples for this study were selected with a focus on visually identifiable production-variations. Samples were collected from catalogue samples (samples labelled as DL06, DL 09, DL 12, DL 18, DL 20, DL 22, see Fig. 2) and from museum objects (samples labelled as DL15, DL 16 and DL 24, see Figs. 3, 4 and 5). Table 2 provides brief information on the samples, whereas Fig. 6 shows the optical images of the cross-sections of the selected samples. All samples demonstrate a multi-layered build-up, varying from 2 to 6 visually identifiable layers (Fig. 6). Typically, they consist of 3 visually different layers (see for example optical images of the samples DL09, DL15, DL16, DL18, DL20 in Fig. 6). Layer 1 represents the core layer (usually more than 1 mm thickness), while layers 2 (circa 0.2 mm) and 3 (less than 0.1 mm) represent the decorative and protective layer, respectively. Samples DL06 and DL22 contain only two layers without a protective layer, while the specific for the latter is the red core layer. DL12 is the most structured, showing different layers of core and decorative layers. Furthermore, it is also two-sided with red decorative layers on both sides.

Material analysis using different spectroscopic techniques was dedicated to the identification of different (inorganic/organic) materials present in different layers (i.e. core, decorative, protective, see Introduction). Table 3 summarises the materials identified through Raman and infrared (FTIR) spectroscopy, arranged according to the different analysed locations of the respective samples which correspond to the numbers on the macrographs in Fig. 6.

Core layers

In all analysed samples, lignin and cellulose were found in the bottom layer (core), using FT-Raman spectroscopy and FTIR spectroscopy (Table 3). Conventional Raman spectroscopy using laser with 785 nm excitation line did not give useful results on the analysis of the core materials as fluorescence obscured the spectra. Figure 7a shows the spectrum obtained using FT-Raman spectroscopy on the bottom layer of sample DL09, identifying cellulose (bands at ~ 1092, 1116, 1382, 1456, 2896 cm^{-1}) and lignin (bands 1606, 1655 cm^{-1}) [20, 21]. The ATR spectra collected in the core layers of investigated samples of laminates reveal common signals (IR bands at ~ 1454, 1428, 1373, 1338, 1159, 1104, and 1030 cm^{-1}), which belong to cellulose as well as to lignin. Specific infrared bands of

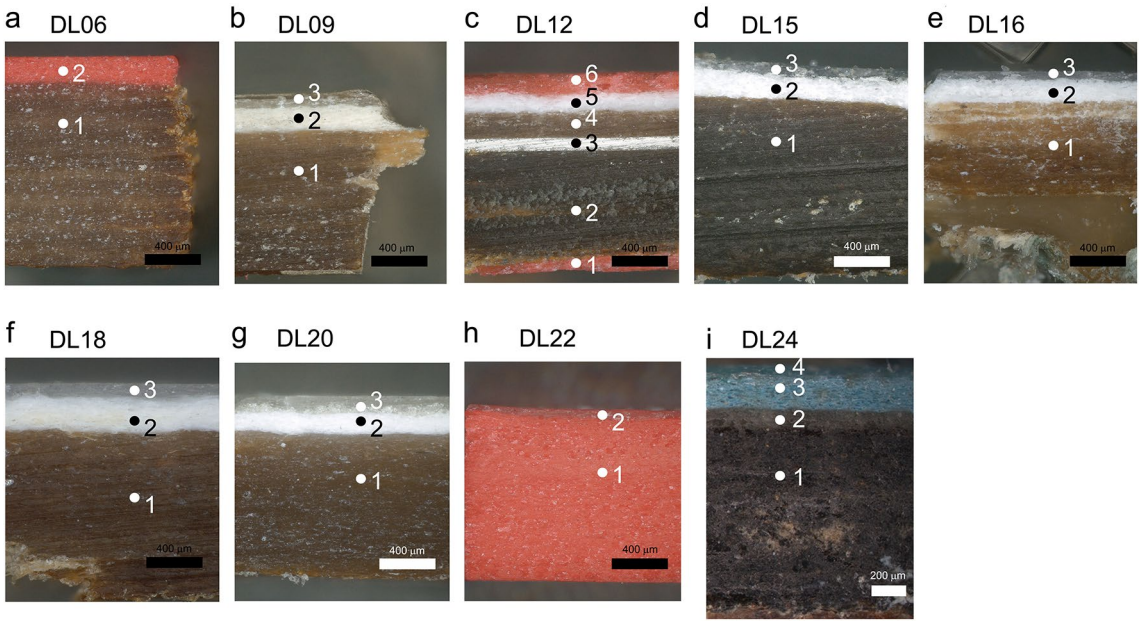


Fig. 6 Optical images of samples with the numbering of the visually identifiable layers: **a** DL06, **b** DL09, **c** DL12, **d** DL15, **e** DL16, **f** DL18, **g** DL20, **h** DL22, **i** DL24 with labelled layers

Table 3 Material identification of the analysed samples

Label	Layer	Results (FT-Raman, micro-Raman, FTIR)
DL06	1	Cellulose, lignin
	2	Melamine formaldehyde resin, Pigment Red 122 (PR112, mono-azo pigment, Naphthol AS), rutile (TiO_2, titanium white)
DL09	1	Cellulose, lignin
	2	Melamine formaldehyde, cellulose
	3	Melamine formaldehyde, cellulose
DL12	1	Melamine formaldehyde, cellulose, PR112
	2	Cellulose, lignin
	3	
	4	Cellulose, lignin
	5	Urea formaldehyde resin, cellulose, thiocyanates
	6	Melamine formaldehyde, cellulose, PR112
DL15	1	Cellulose, lignin
	2	Rutile (titanium white), melamine formaldehyde
	3	Melamine formaldehyde resin, cellulose
DL16	1	Cellulose, lignin
	2	Rutile (titanium white), melamine formaldehyde
	3	Melamine formaldehyde resin, cellulose
DL18	1	Cellulose, lignin
	2	Rutile (titanium white), melamine formaldehyde, cellulose
	3	Melamine formaldehyde, cellulose
DL20	1	Cellulose, lignin
	2	Rutile (titanium white), melamine formaldehyde
	3	Melamine formaldehyde, cellulose, zinc sulphide (ZnS)
DL22	1	Melamine formaldehyde resin, cellulose, lipid component, PR112
	2	Melamine formaldehyde resin, cellulose, lipid component, PR112
DL24	1	Cellulose, lignin
	2	Melamine formaldehyde resin, cellulose
	3	Melamine formaldehyde resin, cellulose, PG8
	4	Melamine formaldehyde resin, cellulose

cellulose are placed at ~ 1316, 1056 cm^{-1} while the bands placed at ~ 1594, 1510, 1263 cm^{-1} are distinctive lignin signals. [22]. The example of spectra containing IR bands of lignin and cellulose are presented in Fig. 8 (layers 2 and 5) for sample DL12. Furthermore, distribution of lignin and cellulose content obtained by FTIR mapping in sample DL12 is presented in Fig. 9b, c, respectively. FTIR mapping showed higher amounts of lignin in layers 2 and 4 (brown layers). On the other hand, cellulose is distributed across layers 1, 2, 4, 5, 6. Pure cellulose (without lignin content) was detected in the top and bottom layer of sample DL12 (Fig. 9b, c). These results corroborate the technical assumptions and written texts, which predict the presence of kraft paper in the core layer. Kraft paper is paper or paperboard produced in the kraft process, and it contains lignin and pectin. Therefore, the detection of lignin was correlated with the use of kraft paper. From the FTIR mapping results, it could be seen, that paper containing lignin (i.e. kraft paper) was not used for the decorative layer (layers 1, 5, 6 on sample DL12), where only cellulose was present. This supports literature which mentions the use of alpha cellulose paper in the decorative layer and overlay [1]. Kraft paper has the function of being strong [23], and in decorative layers, this function is of less importance.

Decorative layers

Melamine–formaldehyde (MF) resin was found in the coloured (decorative) layers, such as layers 2 in sample DL06, DL09, DL15, DL16, DL 18, DL20, layers 1 and 6 in sample DL12 (Fig. 6, Table 3). For example, FTIR mapping also showed the presence and distribution of melamine–formaldehyde (MF) resin (Fig. 7d) in both the red layers (layers 1 and 6) of sample DL12. MF resin

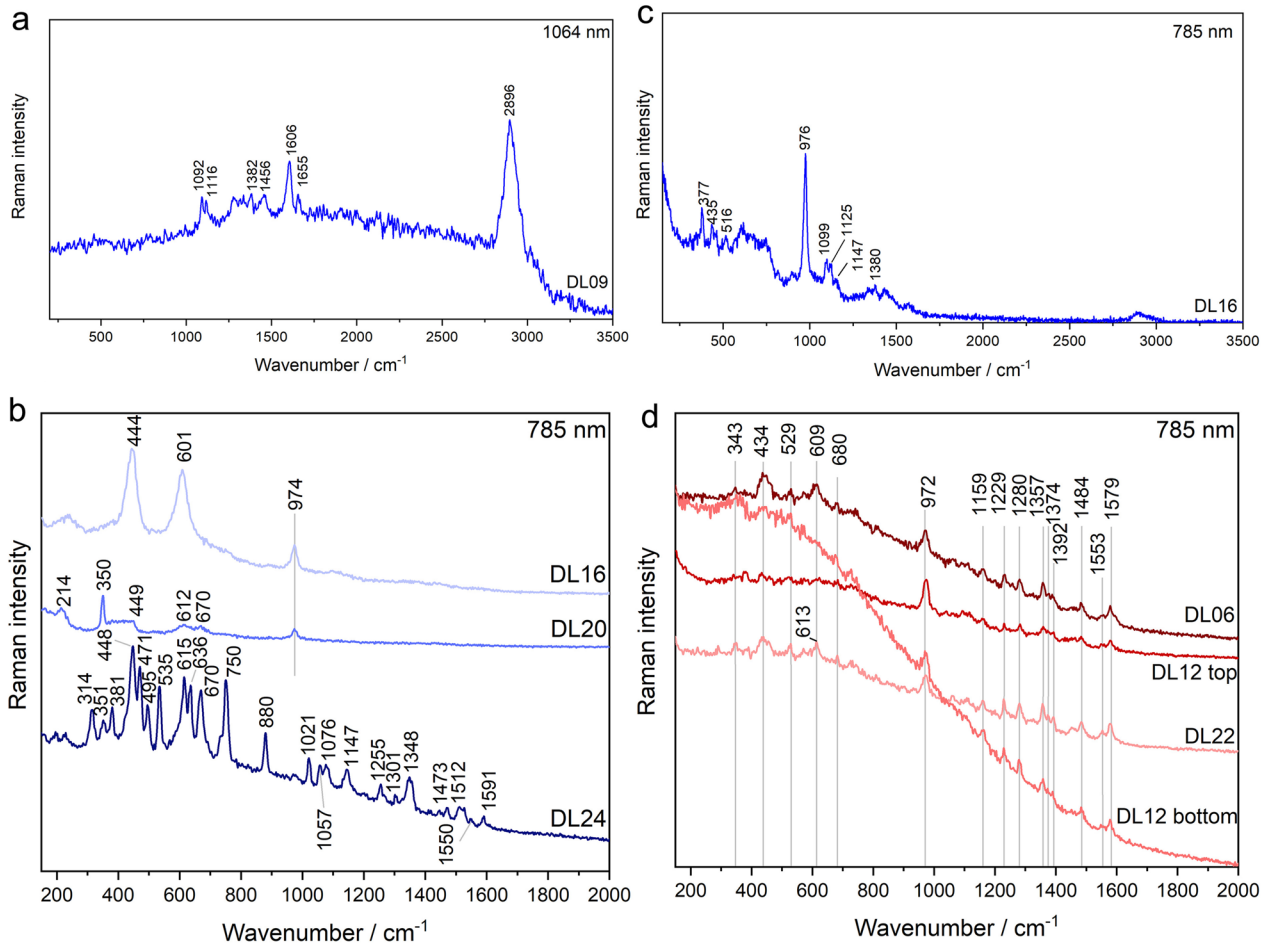


Fig. 7 Raman spectra obtained on different samples; **a** bottom layer of sample DL09, **b** decorative layers of samples DL16, DL20 and DL24, **c** protective layer of sample DL16, **d** red layers of samples DL06, DL12 (top and bottom layers), and DL22

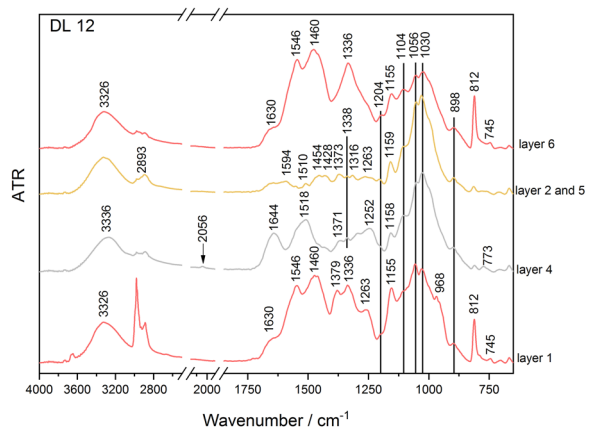


Fig. 8 ATR spectra collected on specific layer of sample DL12

was confirmed by means of FTIR spectroscopy based on its specific IR bands placed at ~ 1630, 1546, 1460, 1336, 1155, 812, 745 cm^{-1} (Fig. 8, layer 1 and 6) [24]. The ATR spectrum collected on layer 1 (sample DL12) reveal an extra signals at 1379 and 968 cm^{-1} that are attributed to vibrations of embedding resin (used for preparation of the samples). FTIR spectrum collected on the red layer of sample DL22 (spectrum not shown) contains, alongside signals of cellulose and MF resin, an additional signal at 1736 cm-1 that can be assigned to a lipid component that was probably used in smaller proportions. The purpose of its presence remains unknown. The presence of lipids could be related to the fact that this laminate was produced for the outdoors, but further investigation was out of the scope of this research.

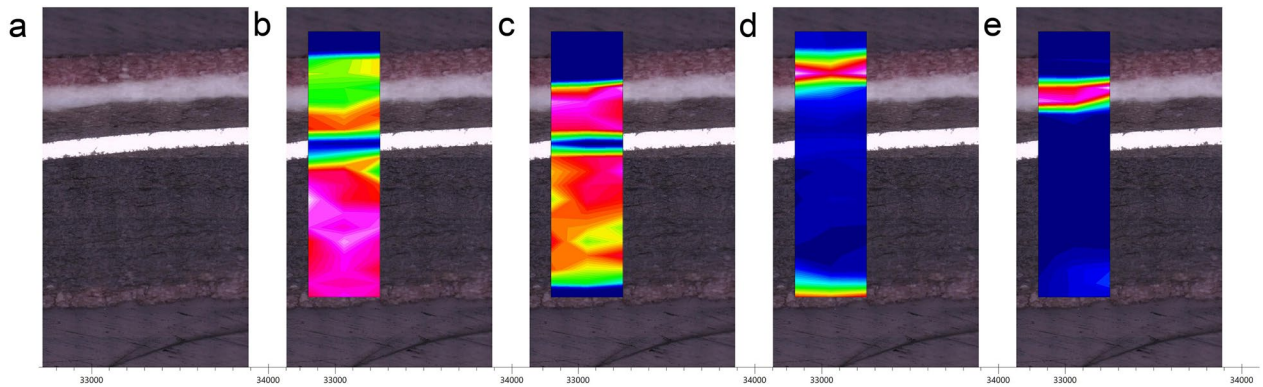


Fig. 9 **a** Optical view of analysed area of sample DL12 and spatial distribution of: **b** cellulose content, **c** lignin content, **d** melamine formaldehyde content and **e** urea formaldehyde resin determined by FTIR mapping. Warmer colours in the correlation maps **b**, **c**, **d**, **e** represent higher content of specific material, while cooler colour tones represent a low content of specific material

Urea formaldehyde (UF) resin was detected in the white layer (Fig. 8, layer 4) of sample DL12, based on specific ATR bands placed at 3336, 1644, 1518, 1458, 1371, 1252, 1158, 1034, 773 cm^{-1} [25]. The ATR spectrum collected on the white layer of sample DL12 also revealed a weakly defined band placed at 2056 cm^{-1} that corresponds to the out-of-phase stretch of a thiocyanate group [26]. Thiocyanates are most likely present in the white layer of sample DL12 as additives. UF resin is most likely present as an impregnating agent, because it was less expensive than MF resin and applied as the first layer whilst preparing the decorative layer before the application of MF resin. However, sample DL12 is the only sample where the presence of UF resin was confirmed.

In the decorative layers, different pigments were found using Raman spectroscopy, such as rutile (samples DL06, DL18, DL15, DL6), zinc sulphide (DL20), PR112-Pigment Red 112-monoazo pigment, Naphthol AS (samples DL06, DL09, DL22), and PG8-Pigment Green 8- azo metal complex, Pigment Green B (sample DL24). Figure 7b shows Raman spectra obtained on decorative layers (layers 2 for DL16 and DL20, and layer 3 for sample DL24, Fig. 6), identifying titanium oxide-rutile based on the bands at ~ 441 and 601 cm-1, zinc sulphide according to the bands at ~ 214, 350, 612, 670 cm^{-1}, and PG8 based on the bands placed at 314, 351, 381, 448, 471, 495, 535, 615, 636, 670, 750, 880, 1021, 1057, 1076, 1147, 1255, 1301, 1348, 1472, 1512, 1550, 1591 cm^{-1} [8, 18, 19]. In addition, in the spectra of the decorative layer of samples DL16 and DL20, the presence of melamine–formaldehyde is also visible (Raman band at ~ 974 cm^{-1}) [27, 28]. It is known that zinc sulphide can exhibit phosphorescence [29] which is possibly a reason that sample DL20 'glows in the dark' (see description of the sample in Table 1).

In comparison, the red samples (DL06, DL12, DL22) analysed with Raman spectroscopy (Fig. 7d) showed the presence of synthetic organic red pigment PR112 in addition to melamine formaldehyde resin (band at ~ 972 cm^{-1}), even though those three samples belong to different decades. More specifically, in the case of DL12, pigment was detected on both sides, in the top and bottom layer, and on sample DL12, titanium oxide (rutile, titanium white) was also found. PR112 was identified using Raman spectroscopy based on the bands at ~ 1159, 1229, 1280, 1357, 1374, 1392, 1484, 1553, 1579 cm^{-1} and weaker bands at lower wavenumber at ~ 343, 529, 613, 680 cm^{-1} [10]. However, the presence of TiO_2 is also suggested for sample DL06 and possibly, also for DL22 due to the broad bands at ~ 434 and 609 cm^{-1}, even though those bands can overlap with the band characteristic of PR112.

Protective layers

In all of the cases (all samples except DL06, DL12, DL20), where the protective layer was visible above the decorative layer (layers 3 on samples DL09, 15, 16, 18, Fig. 6), melamine–formaldehyde resin and cellulose were detected with Raman and FTIR spectroscopy (Table 3). It is known that MF resin serves as a good protection against heat and scratching [4]. For example, Fig. 7c shows the Raman spectra obtained on the protective layer of the sample DL16, identifying cellulose (bands at ~ 377, 435, 516, 1099, 1125, 1147, 1380 cm^{-1}) [10] and melamine–formaldehyde resin (band at ~ 976 cm^{-1}) [27, 28].

Upon looking at the results from a chronological point of view, the literature mentions an initial period (early twentieth century) where various thermosets were used as binding medium, PF (phenol formaldehyde), UF (urea formaldehyde), and with MF (melamine formaldehyde) mentioned as the last new addition in time. But also differences in strengthener were mentioned [2]. The further

along in time, the less variation in composition is mentioned. The results of this study reflect a relatively consistent use of material. MF, cellulose with lignin content (kraft paper), and pure cellulose emerge as the most consistent materials. However, in DL12, also the oldest sample (1953), UF was found which might be related to its manufacturing in the early years of DLs. Interestingly, PF was not detected on any of the investigated samples, even though FTIR seems the proper choice for its detection [30]. Furthermore, the detection of possible additives and/or fillers was only successful in one case (thiocyanates in DL12), probably the concentration of these components is very low and the techniques used in this study were not sensitive enough. Further research employing other techniques, such as chromatography (gas or liquid chromatography), are required in order to obtain more information on the composition of historical decorative laminates.

Conclusion

While most analytical studies focus on contemporary decorative laminates (DLs) to improve them for the current sales market, this article is one of the first to focus on historical DL found in Design Museums and Archives. The multidisciplinary approach of researching the historical source, using optical microscopy, and FTIR (ATR-mapping) and Raman spectroscopy, resulted in a thorough material-technical characterisation of the multi-layered structure of historical decorative laminates.

Raman spectroscopy proved useful for identifying pigments in decorative layers, where the presence of titanium dioxide (rutile, titanium white), zinc sulphide, synthetic organic red pigment PR112, and synthetic organic green pigment PG8 were found on the analysed samples. In the decorative layers, melamine–formaldehyde (MF) resin was detected in addition to cellulose. Furthermore, in one sample the presence also of urea–formaldehyde (UF) resin was confirmed, which was most likely used as an impregnating agent. In the same sample, the presence of thiocyanates was also detected, which were probably added as an additive. It was found that the protective layers are mainly composed of MF resin and cellulose. Moreover, in the lower layers, comprising the core of the laminates, cellulose and lignin were detected suggesting the presence of kraft paper. These results support the historical description on decorative laminates from the second half of the twentieth century; most often they were thought to be composed of several layers of kraft paper, decorative, and protective layer.

A limitation in this study are the few samples from the first half of the twentieth century, which could show more variation given their time of origin and experimentation in the use of materials. Further investigation (using for example advanced chromatographic or other spectroscopic methods) of some unidentified compounds (or compounds in low concentration/traces) be beneficial in this respect to even better distinguish the samples over time.

Abbreviation

FT	Fourier-transform
FTIR	Fourier-transform infrared spectroscopy
PR112	Pigment red 112
PG8	Pigment green 8
MF	Melamine formaldehyde
UF	Urea formaldehyde
PF	Phenol formaldehyde

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Author contributions

KR, LL and AJ developed the concept of the research and drafted the manuscript. KR and LL carried out Raman and FTIR analysis. All authors contributed to data interpretation and writing. All authors read and approved the final manuscript.

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Availability of data and materials

Most of datasets generated and/or analysed during the current study are available in the Zenodo repository, https://doi.org/10.5281/zenodo.7862015. Additional data are available from the authors on reasonable request.

Declarations

Competing interests

The authors declare that they have no competing interests.

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