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EUROPEAN COATED PAPERS, 1850–1975: THEIR IDENTIFICATION FOR CONSERVATION PURPOSES

Keywords: pigment-coated paper, pigment, dye, adhesive, EDXRF, μ-XRD, FTIR-μS, HPLC-DAD-MS

ABSTRACT

The focus of this study is the identification of European machine-coated-paper components: fibres, pigments, dyes and adhesives. The aim is to find proper analytical procedures that will provide paper conservators with a methodological tool to better understand pigment-coated papers, and thus allow them to choose and apply the best possible conservation practice to those objects. A small collection of 12 different objects from the 19th and 20th centuries provided 20 different pigment-coated papers for study. The analytical methods used for material identification were stains, cross-sections, EDXRF, μ-XRD, FTIR-μS and HPLC-DAD-MS. The results confirmed the application of previously published data concerning some coating base white pigments, coloured pigments and dyes, and adhesives. New findings came to light regarding the use of Prussian blue, gold and silver for 19th-century paper coatings. Generally, the results answer the questions of paper conservators regarding the application of analytical methods which the authors hope will support future conservation methodologies.

RÉSUMÉ

L'objet de cette étude est l'identification des composants du papier couché machine européen : fibres, pigments, colorants et adhésifs. L'objectif est de trouver des procédures analytiques adéquates qui doteront les restaurateurs de papier d'un outil méthodologique pour mieux comprendre les papiers couchés, et leur permettra donc de choisir et d'appliquer la meilleure méthode de conservation-restauration possible pour ces objets. Une petite collection de 12 objets différents des xix^e^ et xx^e^ siècles a fourni 20 différentes sortes

INTRODUCTION AND HISTORICAL BACKGROUND

Pigment-coated papers are made of a paper sheet where a fine coating layer is applied either on one side (for decorative and printing coated papers) or on both sides (only for printing coated papers). The production of machine-coated papers started in the1850s (Gunning 1969, Mosher 1968), and the main components of the thin coating layer were and still are white and/or coloured pigments or dyes held together by an adhesive. Depending on final application, different finishes can be applied to modify the surface appearance, with the purpose of achieving a better paper opacity and imparting surface smoothness, gloss, ink absorbency, or to attain different surface features such as embossing or stencil decorations (Busch 1968, Biermann 1996, Gunning 1997, van der Reyden et al. 1993).

This study began with the need for conservation of a collection of European pigment-coated papers encountered on objects from circa 1850–1975. The great variety of coatings featured, either for decorative or printing purposes, was remarkable. Colours ranged from white, blues and greens, to yellows, orange and reds. Pinks, lilacs, maroons, greys, blacks were also found along with some papers with a metallic appearance. Their surface appearance was either plain or embossed with a multitude of patterns (Day 1959).

All pigment-coated paper objects in this study showed variable amounts of surface damage, in the form of stains, fingerprint marks, scratches, abrasion, burnishing, and poor adhesive cohesion of the coating layer, depending on handling and storage conditions they have endured. Micro fissures and deep loss on relief areas were also often seen on embossed motifs. The scant published literature concerning the treatment of these material problems (see for example Baker 1989, Mizrachi 1994, van der Reyden et al. 1993) led to the need for a proper identification of their components, in order to better understand the behaviour of these papers and to establish a methodology for conservation work. A multitechnique analytical approach was used to provide the necessary characterization of 20 pigment-coated papers chosen from 12 paper objects.

PAPER FOR COATING

The paper support layer for coating has differed in composition through time (Prosser 1989). The furnish requirements have been

de papier couché à étudier. Les méthodes analytiques employées pour l'identification des matériaux ont été les tests de coloration, les coupes transversales, la fluorescence X à dispersion d'énergie, la microdiffraction de rayons X, la microspectroscopie infrarouge à transformée de Fourier et la chromatographie en phase liquide haute performance avec détecteurs à réseau de diodes et de masse. Les résultats ont confirmé la validité des données précédemment publiées à propos de certains pigments blancs, des pigments colorés et des colorants, et des adhésifs de l'enduit du papier. De nouvelles découvertes ont été faites au sujet de l'utilisation de bleu de Prusse, d'or et d'argent dans les enduits du xix[e] siècle. D'une manière générale, les résultats répondent aux questions des restaurateurs de papier concernant l'application des méthodes analytiques, et les auteurs espèrent que celles-ci contribueront aux futures méthodologies de conservation-restauration.

RESUMEN

El enfoque de este estudio es la identificación de los componentes europeos del papel recubierto a máquina: fibras, pigmentos, colorantes y adhesivos. El objetivo es encontrar procedimientos analíticos adecuados que proporcionen a los conservadores de papel una herramienta metodológica para comprender mejor los papeles revestidos con pigmentos, y permitirles así elegir y aplicar la mejor practica de conservación posible a dichos objetos. Una pequeña colección de 12 objetos diferentes de los siglos XIX y XX aportó 20 papeles recubiertos con diferentes pigmentos para su estudio. Los métodos analíticos empleados para la identificación de los materiales fueron tinciones, cortes estratigráficos, EDXRF, µ-DRX, IRTF-µS y HPLC-DAD-MS. Los resultados confirmaron la aplicación de datos publicados previamente en relación a algunos pigmentos de base blancos, pigmentos y tintes coloreados, y adhesivos. Se descubrieron nuevos datos en relación al uso de azul de Prusia, oro y plata en los revestimientos de papel del siglo XIX. Por lo general, los resultados dan respuesta a las preguntas de los conservadores de papel relacionadas con la aplicación de métodos analíticos, y los autores esperan que sirva de apoyo para futuros metodologías de conservación.

uniformity, strength resistance to coating application and drying, finish, resistance to printing, folding, bookbinding, and cost effectiveness (Gunning 1969).

The specific properties of the stock (paper composition) vary with mill specifications and end use requirements of the coated paper (Beren 1968). The use of the following pulp types has been reported: esparto grass, deciduous wood (Day 1959, Norris 1952, Prosser 1989), straw and sulphite wood pulp (Norris 1952), kraft wood pulp and soda stocks, mechanical wood pulp, rope, manila (Beren 1968, Busch 1968), chemical pulp and selected waste papers (Gunning 1969 and 1997).

Sizing for these papers can include rosin (Prosser 1989), starch, protein or combinations of these with mineral fillers (Gunning 1969).

PIGMENTS AND COLOUR

Pigments are the basic component of a coating (Busch 1968). They are the first components to be prepared and to them are added further colours as necessary in the form of pigments and/or dyestuffs, followed by adhesives and additives to form the coating.

White coating pigments are generally finer and brighter versions of filler pigments. In coatings they can be used in combination with each other, and abundant formulations were developed over time, depending also on the type of coating machine used.[1] The most common white pigments for coated papers are listed in Table 1.

Table 1
White pigments used for 19th and 20th century paper coatings

Pigment (and other known names)	**Chemical formula**
Alumina trihydrate	$Al_2O_3.3H_2O$
Barium sulphate (baryta, blanc fixe, heavy spar)	$BaSO_4$
Calcium carbonate, natural from calcite or precipitated from aragonite, (chalk, whiting)	$CaCO_3$
Calcium silicate	Ca_2SiO_4
Calcium sulphate (gypsum, pearl white)	$CaSO_4.2H_2O$
Calcium sulphite	$CaSO_3$
Diatomaceous silica (diatomite)	SiO_2
Hydrated calcium aluminium sulphate (satin white)	$3CaO.Al_2O_3.3CaSO_4.31H_2O$
Hydrated magnesium silicate (talc)	$3M_gO.4SiO_2.H_2O$
Kaolinite (China clay, kaolin)	$Al_2O_3.2SiO_2.2H_2O$
Lead white (hydrocerussite, basic lead carbonate)	$Pb_3(CO_3)_2(OH)_2$
Lithophone (Orr's white, Charlton white)	$30\%\ ZnS + 70\%\ BaSO_4$
Potassium titanate	$K_2O.4TiO_2$
Titanium dioxide (rutile or anatase)	TiO_2
Zinc oxide	ZnO
Zinc sulphide	ZnS
Plastic pigments based on polystyrene (since the 1970s)	

Compiled from: Batruk, 1966; Biermann, 1996; Busch, 1968; Day, 1959; Gunning, 1997; Hagemeyer, 1966; Higham, 1963; Labarre, 1952; Lyons, 1966; Mizrachi, 1994; Murray, 1970; Prosser, 1989; Rosenstock, 1966; Russell, 1966; van der Reyden et. al, 1993; Velho, 2003; Roberts, 1996; Willets, 1966a, 1966b & 1970

Colour gives a decorative dimension to coated papers, either by addition of small amounts of coloured pigments and/or dyes to the white mixture, or by ensuring that the entire pigment component of the coating layer is coloured (Busch 1968). A list of coloured pigments is shown in Table 2, and dyes historically applied to pigment-coated papers are described extensively in Landbergé (1966) and Gunning (1969).

Table 2

Colour pigments used for 19th and 20th century paper coatings

Natural Pigments		
	Iron oxides or hydroxides + manganese oxides	
Browns	Raw and burnt umber	
Reds	Iron oxides, burnt sienna	
Yellows	Ochre, raw sienna, natural oxide	
Synthetic Inorganic Pigments		Colour index
Browns	Iron oxide compounds	Pigment brown 6, 7
Reds	Iron oxide	Pigment red 101, 102
	Lead oxide (red lead)	(pigment red 105)
	Basic lead chromate	Pigment red 103
	Cadmium sulphoselenide	Pigment red 108
	Cadmium mercury colours	Pigment orange 23, red 113
Oranges	Cadmium sulphide	Pigment orange 20
	Cadmium sulphoselenide	Pigment orange 20
	Iron hydroxide	Pigment yellow 42, 43
	Basic lead chromate	Pigment orange 21
	Lead chromate molibdate	Pigment red 104
Yellows	Cadmium sulphide	Pigment yellow 37, 35
	Iron oxide	Pigment brown 6, 7
	Iron hydroxide	Pigment yellow 42, 43
	Lead chromate	Pigment yellow 34
Greens	Chrome oxide or hidrated chrome oxide	Pigment green 17
	Phthalocyanine blue + chrome yellow	(blue 15, 16 + yellow 34)
Blues	Ultramarine blue	Pigment blue 29
	Phthalocyanine blue	Pigment blue 15, 16
Blacks	Iron oxide	Pigment black 11
	Carbon black	Pigment black 6, 7
Metallic Pigments		
	Aluminium, powder	
	Copper, powder (acid copper sulphate)	
	Bronze, powder	

Compiled from: Landbergé, 1966; Mosher, 1968; Gunning, 1969

ADHESIVES AND CO-ADHESIVES

The function of the adhesives used is to cohere the coating mixture, to fill the voids between pigment particles and to provide bonding strength between the coating and the paper layer. Co-adhesives may be used to increase dimensional stability, flexibility, wet-rub resistance, smoothness and provide better ink hold-out. In the context of pigment coated papers, adhesives and co-adhesives can be either water based natural materials, including starches (corn in USA, wheat in Canada, tapioca, white and

Figure 1
Sewing box, 1870s, probably of French origin

Figure 2
Sewing box detail showing yellow embossed, green, gilded embossed and dark blue embossed pigment-coated papers

Figure 3
Sewing box silvered paper embossed pattern detail

sweet potato in Europe, sorghum, rice and manioc in Asia), gum arabic and protein (animal glue, casein from cow's milk, gelatine, carboxylated soy bean), or, since the 1940s, synthetic emulsions such as polyvinyl alcohols, synthetic resin lattices as styrene-butadiene rubber (SBR), acrylates and polyvinyl acetate lattices (PVAc), and other synthetic adhesives, such as methylcellulose, carboxymethylcellulose, hydroxyl ethyl cellulose and polyvinyl pyrrolidone, amongst others (Biermann 1996, Busch 1968, Gunning 1997, Loomer 1970, Mizrachi 1994, Mosher 1968, Prosser 1989, Roberts 1996, van der Reyden et al. 1993).

DESCRIPTION OF OBJECTS AND PIGMENT-COATED PAPERS EXAMINED

Twelve different objects were divided in two groups based on their probable production dates: a first group of four from the 19th century and a second group of eight from the 20th century.

The first group includes a sewing box from the 1870s (probably French) (Figures 1–3), a decorated gift box (Figures 4 and 5), a fan box of unknown origin and a flyleaf from a British alphabet book. The second group comprises three jewellery boxes (orange, white and red, respectively, Portuguese), two multipurpose boxes (blue and yellow, respectively, Portuguese), a 1930s Molinard concrete French perfume box, and a small wedding menu card probably from the 1940s (Portuguese).

The coating colours of the papers ranged from white (four), blue (three), green (two), yellow (two), orange (one), red (two), pink (three), purple (one), and two metallic examples giving a total of 20 pigment-coated papers to analyse. The embossing shapes so far found in this research range from floral and geometrical patterns, to anthropomorphic motifs, and leather imitation. A similar range of embossing types was noted by Day (1959).

TESTING ANALYSIS AND DISCUSSION

The analytical methods used were microchemical tests, energy dispersive X-ray fluorescence spectrometry (EDXRF), micro-X-ray diffractometry (μ-XRD), light microscopy of cross-sections, Fourier-transform infrared microspectroscopy (FTIR-μS), and high-performance liquid chromatography diode array detection mass spectral analysis (HPLC-DAD-MS).

Paper layer analysis

For the fibre analysis Lofton-Merritt and Herzberg stains were used (Browning 1977, Chiaverina 1965, Hortal 1993). The white coated paper from the sewing box allowed the removal of a clean and extremely thin (less than 1 mm) sample using a scalpel. After fibre separation procedures, the sample was stained with a reagent and observed using a Leitz WETZAL compound optical microscope. Only rag paper was identified from this artefact. It was decided not to attempt fibre analysis of the other papers as the risk of visible damage to the artefacts was considered to be too great. It was also felt that the particular fibres used had only minor relevance to the behaviour of the coatings themselves.

COATING LAYER ANALYSIS

EDXRF is widely used in scientific studies due to its non-destructive character, essential when the priority is maintaining the integrity of the objects. This technique allowed a first qualitative and quantitative elemental composition determination of the coatings.

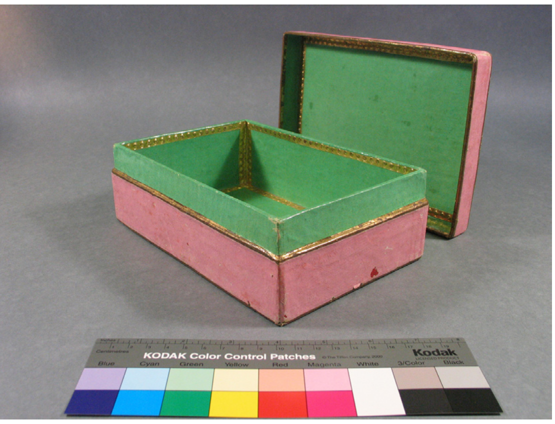


Figure 4
Decorated gift box, 19th century

Figure 5
Pink embossed pigment-coated paper detail from gift box

The unit used was a portable model XRS38 from EIS Sarl.[2] Each paper was analysed using voltages within the range 25 to 30 kV, a current of 0.3 mA, and scan time of 300 seconds. The 20 pigment-coated papers test results (Table 3) showed: a) gold application for the gilded paper applied over a red bole layer; b) silver, for the silvered paper, probably with no underlying white pigment coating layer; c) the predominance of barium sulphate (baryta) on 20th-century coatings; and d) the prominent presence of lead on several papers, especially on 19th-century ones, a probable indication of white hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) and/or a coloured lead pigment.

The small size of the objects allowed a direct μ-XRD analysis of the coatings using a Bruker D8 Discover diffractometer equipped with Cu Kα radiation, a Göbel mirror assembly, and a GADDS detector,[3] with a 40 kV working voltage, 40mA current intensity, and a signal acquisition time of 900 seconds. The results (Table 3) show that this technique was able to validate data from the EDXRF, in particular the presence of gold with red ochre and silver, and confirmed the trend for hydrocerussite/cerussite to be used for 19th-century coatings. It also corroborated increased use of baryta in 20th-century coatings (van der Reyden et al. 1993), and identified lead oxide (minium) in red and orange coatings, hematite purple in purple coatings, and Prussian blue and lazurite in blue coatings. It did not answer questions regarding the possible presence of cinnabar in the Molinard perfume box and which components gave colour to pinks, greens and yellows.

The purpose of mounting cross-sections of the coated papers was observation and measurement of paper and coating thicknesses, as well as to prepare samples for FTIR-μS characterization. Scalpel cut 1 mm thin longitudinal samples of some of the pigment-coated papers were prepared, and each was mounted in the centre of moulds with a drop of cyanoacrylate glue. The moulds were filled with epoxy resin Epofix[4] and left to dry for 24 hours, after which the exposed sections were polished prior to observation with a Leitz WETZAL compound optical microscope.

Cross-sections were obtained from all of the pigment-coated papers, except for those where sample extraction would have caused unacceptably visible damage. The results show that the coating thickness for 19th-century coated papers ranged from 50 μm (for plain papers) to 80 μm (for gilded

Table 3

EDXRF and µ-XRD analysis results of pigment-coated papers

Objects (date)	Coated Paper Colour	EDXRF Results	µ-XRD Results
Sewing Box (1870s)	Dark blue, embossed	Fe > Pb > Cu > K, Ca > Si > S > Ti or Ba, Mn	Cellulose, iron cyanide, cerussite, kaolinite, gypsum, quartz
	Pale blue	Cu >> Fe > Ca > Pb > S > Cl, K, Ti or Ba, Mn	Cellulose, hidrocerussite, cerussite, calcite, lazurite, talc
	White, embossed	Pb >> Ba > Ca, Fe > S, Cl, Cu	Cellulose, hidrocerussite, cerussite, talc, barite
	Silvered, embossed	Fe > Ag > Ca > Pb > S, Cl, Mn	Cellulose, silver
	Gilded, embossed	Cu > Fe > Au, Pb > Ca, Ti > S, K > Mn	Cellulose, gold, hematite, cerussite, kaolinite, quartz
	Yellow, embossed	Pb >> Fe > Cu > S, Cl, Ca > Si	Cellulose, + pigment not yet identifyed
Gift box (end 19th cent.)	Pink, embossed	Pb > Ca > Fe > Hg > S, Cl > K, Mn	Cellulose, hydrocerussite, cerussite, gypsum, quartz, talc
	Green	Cu > As, Pb > Cr, Ba > Ca, Fe > S > Cl, K	Cellulose, barite, gypsum, calcite
	Red, embossed	Pb > Fe > Hg > Ca > S, Cl > K, Mn	Cellulose, minium, barite, quartz, kaolinite
Fan box (end 19th cent.)	Pink	Ca > Fe > K > Mn > P, S > Si, Cl	Cellulose, calcite, gypsum
	Green blue	Cu >> Ca > Fe > S, K > Cl	Cellulose, calcite, gypsum
Flyleaf from book (end 19th cent.)	Purple	Fe > Ca > S, K, Pb > Si, P, Ti ou Ba, Mn > Cl	Hematite, quartz, gypsum
Blue box (20th cent.)	Dark blue	Fe > Ba > Ca, Zn > S > K > Mn > Si > P, Cl	Lazurite, barite
Orange jewellery box (20th cent.)	Orange, embossed	Pb > Ca > Mg > K > Fe > S, Cl	Minium
Yellow box (20th cent.)	Yellow	Ba > Fe > K > Si, S, Ca, Mn > Pb >Al, Cl	Barite, kaolinite
White box (20th cent.)	White	Ba >> Zn > S, Fe > K, Ca > Si, Cl	Barite
White jewellery box (20th cent.)	White, embossed	Ca >> Fe > S > Mn > P, Cl, K	Cellulose, gypsum
Red jewellery box (20th cent.)	Dark pink, embossed	Ba > Fe > Zn > Ca > S > K, Sr > Cl	Barite, calcite
Molinard concrete perfume box (1930s)	Red, embossed	Ba > Fe > Ca > Pb > Zn, Sr > S, K, Mn > Si, Cl	Barite, cinnabar (?)
Wedding Menu (1940s?)	White	Ba >>S, Sr > Cl, Ca > K, Fe	Barite

embossed papers), and the paper thickness ranged from 80 µm (for plain papers) to 130 µm (for gilded embossed papers). The coating thickness for 20th-century coated papers ranged from 40 µm to 50 µm, and the paper thickness ranged from 100 to 200 µm (regardless the existence or not of decorative three dimensional effects). These differences are probably due to improvements made in machinery and materials composition over time. Combined with previous data, the technique also showed that the orange coating was not a mixture of white and coloured pigments, but a one-colour pigment component, possibly with a pre-coating layer or adhesive migration (Figure 7) (Busch 1968). On examination of the gilded coated paper cross-section gold specks of leaf were clearly visible over the red ochre bole layer (Figure 6). Cross-sections confirmed a one-side coating for decorative pigment-coated papers and a two-sided coating for printing papers (Figures 6–8).

FTIR-μS analysis was performed using a Nexus 670 FTIR spectrometer coupled to a Nicolet ContinuμmTM microscope by Thermo NicoletTM.[5] For each sample 256 scans were recorded with a resolution of 4 cm^{-1}. The results confirmed results given by μ-XRD, but in addition detected Prussian blue on the pale blue coating of the sewing box, white lead on the white coated paper of the sewing box and hydrated magnesium silicate (talc) as the white component for the yellow coated paper on the sewing box. Regarding adhesives, FTIR detected spectrum peaks between 1541-1552 cm^{-1} and 1643-1652cm^{-1} characteristic of the presence of protein (1550 and 1656 cm^{-1}), possibly from hide glue (Baker et al. 1989) in the four samples tested so far, corroborating its use for earlier produced pigment-coatings (Prosser 1989). Further analysis on these and the adhesives of other samples remains to be performed.

Small (1 mm^2) samples were taken from surface of the coatings for HPLC-DAD-MS analysis. An Agilent 1100 Series system was used together with a Lichrocart Purospher Star RP-18 5 μm 250×4.6 mm column. HPLC-MS experiments were carried out using a triple quadrupole mass spectrometer Quattro LC (Micromass, Manchester, UK), equipped with an electrospray ion source (ESI) operating in positive mode at 3 kV capillary voltage and a cone voltage of 50 V. The results were all inconclusive, probably due to sample size. Nonetheless, results indicated the presence of dyes in some of the coatings (Landbergé 1966, Mosher 1968, Gunning 1969), so further tests will be performed on larger samples in order to further assess the potential of this method.

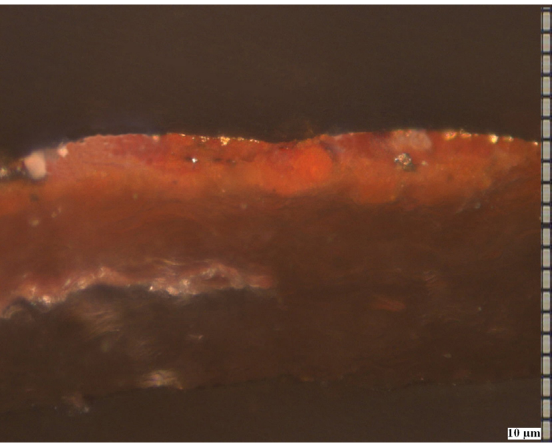
The final test results are summarised on Table 4.

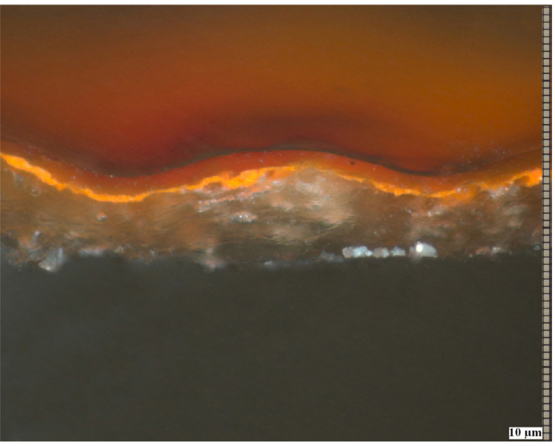
CONCLUSIONS

Overall the analytical methods used for material identification corroborated each other's data. The combined results show variations in material composition between pigment-coated papers (Table 4) probably due to variations in date, techniques and the particular mills which produced the papers.

With regard to white pigments used in coatings, the most commonly found during this study were barium sulphate (detected in ten coatings, six from the 20th century), followed by calcium sulphate (seven coatings, six from the 19th century), calcium carbonate (five coatings, four from the 19th century), lead white (five coatings, all from the 19th century), hydrated magnesium silicate (four coatings, all from the 19th century) and kaolinite (three coatings, two from the 19th century). None of the others listed in Table 1 were detected.

Concerning the coloured coatings components, Prussian blue and Ultramarine blue were the pigments used for blue coatings, and lead and iron oxides for





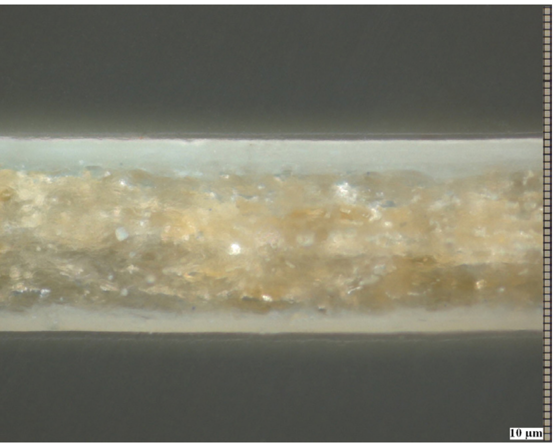


Figure 6
Cross-section from sewing box gilded embossed coated paper. Some minute golden specks can be seen shining on top of the red ochre pigment layer

Figure 7
Cross-section from orange jewellery box one-side pigment-coated paper, where the thin bright orange layer between the coating and the paper can be observed

Figure 8
Cross-section from wedding menu. Notice the two-sided uniform white pigment coating layers, characteristic of printing coated papers

Table 4

Final results of pigment-coated papers analysis (by coated papers colour)

Coated Paper	Objects	White pigments						Adhesive	Colour
		Lead white	Kaolinite	Calcium sulphate	Barium sulphate	Calcium carbonate	Hydrated magnesium silicate		
Gilded, embossed	Sewing Box (1870s)	✓							Gold + Red ochre
Silvered, embossed	Sewing Box (1870s)	not detected							Silver
Dark blue, embossed	Sewing Box (1870s)	✓	✓	✓				Protein	Prussian blue
Dark blue	Blue box (20th century)				✓				Ultramarine blue
Pale blue	Sewing Box (1870s)	✓		✓		✓	✓	Protein	Prussian blue + Ultramarine blue
Green	Gift box (end 19th century)			✓	✓	✓			Not identifyed
Green blue	Fan box (end 19th century)			✓		✓			Not identifyed
White, embossed	Sewing Box (1870s)	✓			✓		✓	Protein	n.a.
White	White box (20th cent.)				✓				n.a.
White, embossed	White jewellery box (20th cent.)			✓					n.a.
White	Wedding Menu (1940s?)				✓				n.a.
Yellow, embossed	Sewing Box (1870s)						✓	Protein	Not identifyed
Yellow	Yellow box (20th cent.)		✓		✓				Not identifyed
Orange, embossed	Orange jewellery box (20th cent.)	not detected							Lead oxide
Red, embossed	Gift box (end 19th century)		✓		✓				Lead oxide
Red, embossed	Molinard concrete perfume box (1930s)				✓				possibly cinnabar?
Dark pink, embossed	Red jewellery box (20th cent.)				✓	✓			Not identifyed
Pink, embossed	Gift box (end 19th century)	✓			✓		✓		Not identifyed
Pink	Fan box (end 19th century)			✓		✓			Not identifyed
Purple	Flyleaf from book (end 19th cent.)			✓					Iron oxide

n.a. - not applicable

reds, orange and purple coatings. The positive identification for Prussian blue positive identification was unexpected. For pinks, yellow and green dyes are possibly present, but further HPLC-DAD-MS analyses need to be carried out to confirm these suppositions. The possible presence of dyes in the coatings is a clear indication of the extra care that these papers require during exhibition and storage.

The detection of silver and gold in the 1880s' sewing box metallic coated-papers was unexpected, since they are costly materials for normal application on paper. This possibly could only have happened during the first years of production of machine made coatings, as an industry trial imitating gilded wood surfaces, for paper to be applied to a very expensive object. It is possible that the so called "sewing box" is a "jewellery box" instead.

The evidence found for protein-based glue tallies with references in the literature to its use as a binder in the early machine paper coatings. This may explain their sensitivity to abrasion and the deterioration of their cohesion and adhesion properties with implications for future preservation methods. Further tests need to be carried out on other samples to explore these questions.

Analytical techniques such as μ-XRD proved to be very effective for pigment identification when used on their own, but for a complete characterisation of pigment-coated papers a multi-technique analytical approach is needed. Further research, as well as continuing to utilise the techniques mentioned above, will also assess the analytical effectiveness of other approaches including the use of scanning electron microscope/energy dispersive spectrometry (SEM/EDS) and polarised light microscopy (PLM). Further research will also consider the cost effectiveness and ease of application of different analytical techniques and how the results obtained can help conservators to make appropriate conservation decisions for objects made using machine made coated papers.

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NOTES

1 Air knife, blade, brush, cast coater, dip coater, gravure coater, knife coater, reverse roll, and transfer roll coater are some of the most important coating machines (Beren 1968, Biermann 1996, Booth 1970, Busch 1968, Day 1959, Higham 1963, Labarre 1952, Roberts 1996).

2 The measurement head is composed of an X-ray tube with a tungsten anode, and a silicon drift detector (SDD). Installed software is MCA 8000A specific for Windows. The focus is achieved by two lasers at a 90º angle, and the area analysed is placed circa 1.5 cm distance from the laser detector.

3 A 1-mm-diameter pinhole collimator was used. The angular range (2θ) was scanned from 6.2 to 71.6° at a step size of 0.02°. Phases were identified using the Joint Committee on Powder Diffraction Standards International Centre for Diffraction Data (JCPDS-ICDD) diffraction database and Bruker EVA software.

4 Epofix resin, code EPOFI Cat. No 40200029, from Struers A/S Pederstrupvej 84 DK-2750 Ballerup, Dennmark.

5 It was used the range 600-4000 cm-1, with an IR source, KBr beam splitter and a DMCT detector for MIR measurements.

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