Considerations about foxing stains in three paper collections ranging from the 16th to the 20th century

Considerações sobre manchas de *foxing* em três colecções de papel dos séculos XVI a XX

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Abstract

Three surveys on the occurrence of foxing stains were carried out on papers dating from 1560 to 1975 in three Portuguese collections. Foxed papers were found to be more intensely and intrusively stained in certain time periods of each collection. Based on historical data and the professional paper conservation expertise, the authors linked the increased occurrence of foxing stains in certain time periods to the new papermaking processes and materials, which began to be introduced in the late 18th century, and in particular to a synergistic effect between three factors: the use of deficient gelatine sizing which began to present a poorer quality and homogeneity, the presence of iron-containing impurities throughout the paper leaf and a distinct absorbency of moisture. Observing batches of morphologically similar papers by using photographic imaging with different types of light sources and incidences, the authors verified that similar papers present similar foxing stains.

KEYWORDS
Foxing stains
Papermaking
Conservation surveys
MNAA museum
MBP museum
BNP library

Resumo

Foram efetuados levantamentos sobre a ocorrência de manchas de *foxing* em papéis de 1560 a 1975 em três acervos nacionais. Observou-se, em cada um dos espólios, que certos períodos de tempo apresentavam um surgimento mais intenso e intrusivo dessas manchas. Com base em informação histórica e na experiência profissional na área da conservação de papel, os autores relacionaram este facto com novas tecnologias e materiais usados no processo de produção de papel a partir do último quartel do século XVIII e, particularmente, com a possibilidade de existência de um efeito sinergético entre a diminuição de qualidade ou falha de uniformização da encolagem de gelatina, a presença de novos procedimentos ou aditivos ricos em impurezas contendo iões ferro e uma sorbência irregular de humidade na folha. Também verificaram, através de imagens fotográficas com diferentes incidências e tipos de radiação, que grupos de papéis morfologicamente semelhantes apresentam manchas de *foxing* também semelhantes.

PALAVRAS-CHAVE
Manchas de *foxing*
Fabricação de papel
Levantamentos de conservação
Museu MNAA
Museu MBP
Biblioteca BNP.

Introduction

Foxing studies have been developed since the 1930s [1]. Different causes had for a long time divided authors opinions' on the hypotheses for the occurrence of foxing stains, either contemplating local oxidation of cellulose catalysed by metal (iron or copper) ions or as a result of the vital activity of microorganisms (fungi and/or bacteria). Ligterink et al. [2] contributed to the discussion by suggesting that local accumulation of moisture was probably connected to the formation of foxing and shortly afterwards several authors [3-5] confirmed discolouration developing by a wet-dry interface mechanism. Studies from Choisy and co-workers [6] and Bicchieri and co-workers [7], using infrared spectroscopy, observed that foxing stains contained chemical groups indicative of cellulose oxidation such as double or triple carbon bonds and carbonyl or carboxyl groups. Since then, the interest in foxing has resurged using new analytical instrumentations that help to pile up stones in a search for a consensual theory as to the reasons for the formation of the stains.

Foxing research from the last six years has undoubtedly linked fungal activity to foxing stains [8-16]. Some of these authors [9-10] have also reported a clear increase in porosity and humidity in the interior of the foxing stains. Sclocchi and co-workers [16], on a study on gelatine-silver foxed photographs, added new insight to the foxing question by documenting a close interaction between the microorganisms and the inorganic materials used in the items' production and proposing that the appearance of the stains depended from the settlement and growth of halotolerant fungi and bacteria that produced localized hot spots of organic material on gelatine. Nevertheless, it is still not clear if the fungal presence found associated with the oxidized foxing spots is the cause of it or an opportunistic biotic development after the formation of foxing [10].

In the first half of the twentieth century, iron salts were considered to be a stimulant for the fungal growth [17-18]. Some studies evaluating the iron and copper contents on foxed papers have not been able to detect local differences between foxed and unfoxed areas [19-21]. However, Barrett [22] in his analysis of residual elements in historical papers found that papers in poor condition had a higher overall content of iron, copper, sulphur, chlorine, potassium and aluminium. More recently, Bertalan's [23] study on modern papers proposed an alternative explanation for foxing, enlightening the chemical nature of inorganic additives over cellulose or sizing. Foxing may be caused by inorganic additives' polymerization in and on paper.

Based on historical data and on our empirical experience, we put forward the hypothesis that similar papers tend to develop similar foxing stains and there seems to exist a synergetic effect between three factors as the major cause for foxing incidence in the paper substrate: the use of less impervious gelatine sizing film, the general presence of iron-containing impurities throughout the paper leaf due to contamination from the papermaking process, and a differentiated absorbency of moisture resulting from several factors, being the growth of fungi within the foxing stains no more than an opportunistic act. This idea formed itself from surveying different collections and time periods during foxing stains' projects, established between the Portuguese National Conservation Organism, Laboratório José de Figueiredo, and Centro de Física Atómica, between 2007 and 2010 [19-24], and from 2012 until the present with Laboratório HERCULES [20-21, 25]. An analytical approach based on different characterization techniques was used during these projects for the study of foxing stains in a small group of samples from the surveyed collections discussed in this work. One interesting aspect was that the authors did not find an increase in iron content in the stains when compared with the unstained paper support [19-21]. Nevertheless, this does not exclude that the paper leaf can be overall contaminated by transition metal ions-containing impurities, namely iron-containing impurities, even in very low percentage, that can act as catalysts for the oxidation of cellulose in a certain moment of the foxing stain formation process. It was out of reach to analyse the entire surveyed collections due to their size. A different approach based on the visual observation of large collections of works and lap of time was then sought. The work herein presented includes the results of the surveys carried out on three Portuguese institutions and some laboratory work based on visual observation and digital imaging under different illuminations of selected batches of papers.

Methodology

Collections' survey

In order to evaluate the extent of foxing stains on historical items of Portuguese cultural heritage, surveys were carried out on Portuguese artists' paper drawings from the sixteenth century to the early nineteenth century at Museu Nacional de Arte Antiga (MNAA), on a collection of preparatory drawings and printed magazine folios; from the late nineteenth century at Museu Bordalo Pinheiro (MBP); and on a newspaper collection from 1835 to 1975 at Biblioteca Nacional de Portugal (BNP). It is not possible to estimate if the papers are of Portuguese origin or not since most of them do not present watermarks. Nevertheless, until the second half of the nineteenth century, drawing papers were mostly imported from Italy, France and Holland while the lower-quality papers from the later periods, like the ones used in Bordalo Pinheiro's works, may be from Portuguese origin. Each collection was divided into different classes, according to the typology and frequency of foxing incidence. In the case of the MBP collection, the publication periods were also taken into account. Once again, the professional expertise in the area of paper conservation was fundamental for deciding how the objects should be grouped.

The MNAA survey was performed in the scope of the research project *Morphological characterization of paper stains and treatment methodologies* developed, as stated before, by the partners Centro de Física Atómica and Laboratório José de Figueiredo [24]. The aim of this project was to study stain incidence on drawings from the sixteenth to the nineteenth century. The survey included only loose paper drawings from Portuguese's artists and a total of 1568 drawings from 1560 to 1850 were analysed (Table 1). This interval of time was divided into four different periods, according to the greater or lesser incidence and morphological features of foxing. The first period, from 1560 to 1619, had a total of 46 drawings; the second period, from 1620 to 1775, comprised 419 drawings; the third period, from 1776 to 1825, totalled 1039 drawings; and the last period, from 1826 to 1850, 64 drawings.

The MBP survey dealt with a small portion of the works of Rafael Bordalo Pinheiro (1846-1905) who was a nineteenth-century Portuguese artist renowned for illustrative and sarcastic caricature drawings that he published with a political or social message in humoristic magazines. His museum deposit holds over 3500 works on paper, which have been subjected to very similar environmental conditions since the official opening of the museum in 1924. Not being able to study the entire paper collection, the authors decided to concentrate on the preparatory drawings and lithographed reproductions on printed folios from the humoristic journal *António Maria*. The lithographed reproductions on printed folios will be herein abbreviated to printed folios. This journal had two publication periods: from 1879 to 1885 and from 1891 to 1898, with a total of 925 paper folios (Tables 2 and 3).

Wanting to see how foxing occurred in a wide lag of time for newsprint papers, the oldest Portuguese newspaper publication, founded in 1835, *O Açoriano Ocidental*, was selected to be studied from the BNP Library newspaper collection. Although this newspaper continues to be published, the survey stopped at the end of 1975, totalling a quest for foxing stains in 8040 newspaper folios. This survey, from 1835 to 1975, was divided with the same criterion of the MNAA survey that is, in four different periods according to foxing incidence (Table 4). The *O Açoriano Ocidental* collection is not complete, lacking some time periods.

Table 1. Distribution of foxing stains on the MNAA drawings' collection.

Time period	Surveyed		Affected by foxing	
1560-1619	46	2.9 %	20	43.5 %
1620-1775	419	26.7 %	33	7.9 %
1776-1825	1039	66.3 %	241	23.2 %
1826-1850	64	4.1 %	10	15.6 %
Total	1568	100 %	304	19.4 %

Table 2. Distribution of foxing stains on the MBP printed folios' collection.

Time period	Surveyed		Affected by foxing	
1879-1885	405	65.2 %	74	18.3 %
1891-1898	216	34.8 %	3	1.4 %
Total	621	100 %	77	12.4 %

Table 3. Distribution of foxing stains on the MBP drawings' collection.

Time period	Surveyed		Affected by foxing	
1879-1885	53	17.4 %	22	41.5 %
1891-1898	251	82.6 %	39	15.5 %
Total	304	100 %	61	20.0 %

Table 4. Distribution of foxing stains on the BNP newspaper´s collection.

Time period	Surveyed		Affected by foxing	
1835-1867	828	10.3 %	221	26.7 %
1871-1903	647	8.1 %	45	7.0 %
1907-1923	1593	19.8 %	58	3.6 %
1924-1975	4972	61.8 %	2	0.0 %
Total	8040	100 %	326	41.4 %

Morphological characterization of selected foxing stains

An empirical consideration that came out from the survey was that similar papers tend to developed similar foxing stains. In order to better evaluate this statement, five batches of three similar papers each (groups of papers whose texture, tone, thickness and optical imaging are closely the same) with similar foxing stains were selected for morphological characterization: three belonging to the MNAA collection (batches A, B and C) and two from the MBP collection (batches D and E). No papers were chosen from the BNP newspaper collection due to their book format and fragile mechanical properties. Batch A corresponds to three drawings from Wolkmar Machado on thin white laid paper, with 24 mm chain line spacing and similar thickness and surface texture. Batch B consists of three drawings from Domingos Sequeira on thick white wove papers, two of equal thickness, and all with very similar surface texture and tone. Batch C's drawings, from the same artist as in batch B, are portraits from parliament deputies on medium wove, brown/green toned, tinted paper of very similar thickness and surface texture. Batches D and E correspond to drawings from Bordalo Pinheiro: batch D is an example of very similar thin printed folios that have been attached to a blue writing paper used as secondary support; batch E, made up of drawings of similar wove white medium-thick papers, also had the same stain development.

The papers were observed under reflected and transmitted light and UV radiation using a Nikon Coolpix P520 camera placed on a column stand. The camera was set for macro focus and the images captured on automatic mode using the same focal distance. A UV Waldmann W portable device with two TL4 W/08 F4T5/BLB Philips lamps was used as a UV radiation source.

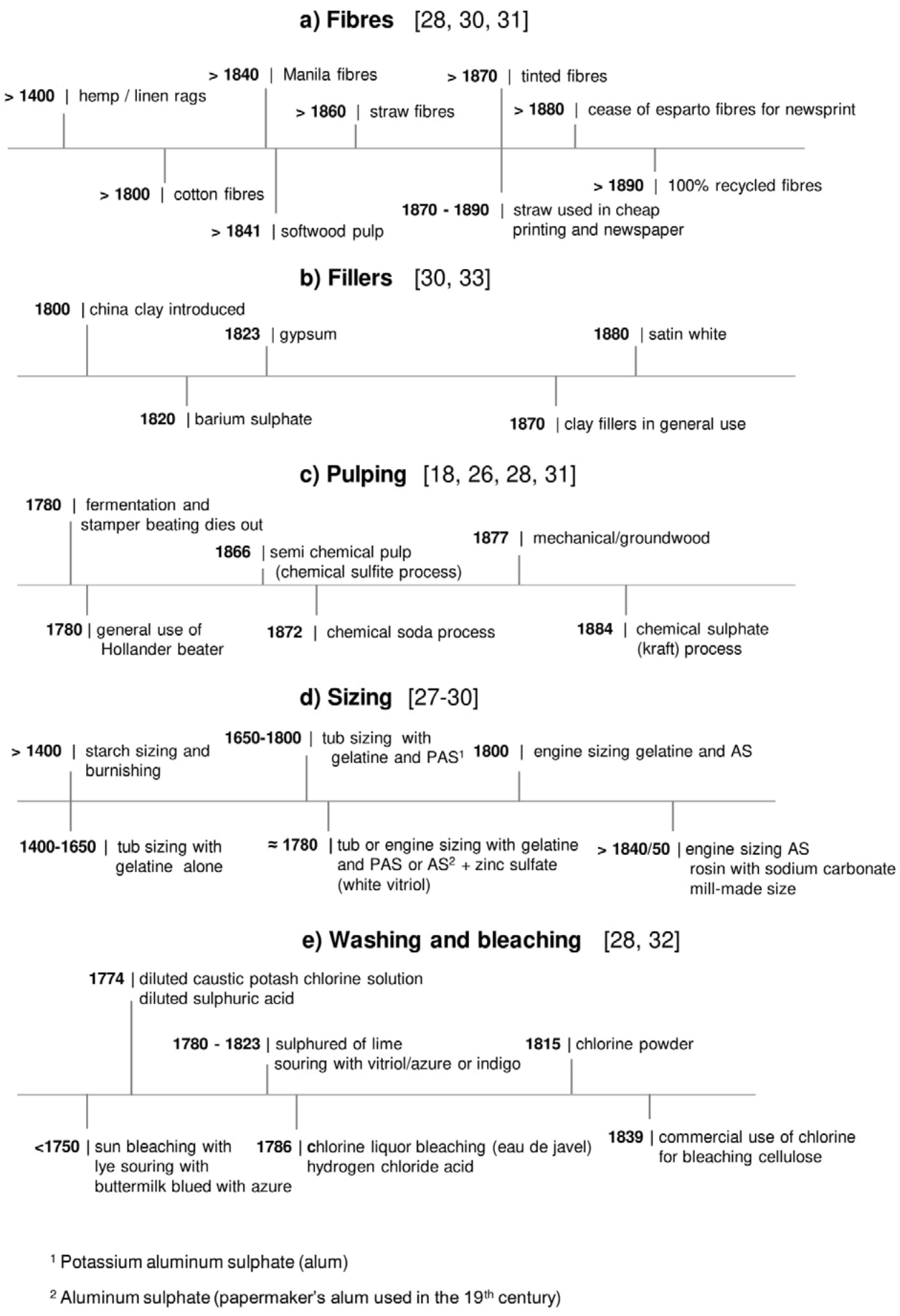

Figure 1. Timelines for papermaking historical technologies [18, 26-33]: *a)* fibres; *b)* fillers; *c)* pulping; *d)* sizing; and *e)* washing and bleaching.

Results and discussion

Collections' survey

One interesting aspect that came out from the survey was that none of the collections had, until the end of the twentieth century, climate-controlled storage conditions, but foxing stains developed mostly on certain papers. The possibility reported in the literature on the usual occurrence of foxing in papers that were stored in conditions with relative humidity and temperature higher than recommended (65-95 % and above 20 °C, respectively) does not seem to have played a fundamental role in the development of foxing stains in these collections.

In order to discuss possible causes for the foxing incidence, historical data [18, 26-33] on papermaking technologies and constituents that were in use in the time period considered in this study was employed to construct the timelines presented in Figure 1. These timelines only intend to account for the probable dating of the technical situation, especially regarding the change of equipment. For example, the Hollander beater, which was invented in the mid-seventeenth century, only spread throughout Europe in the mid-eighteenth century and to America in 1780 [26, 28].

For the subsequent discussion, other aspects referred in the literature should also be considered, namely the fact that certain papers develop more foxing stains than others; drawing, printing and newsprint papers were manufactured with different raw materials and manufacturing procedures and each of these paper categories could use fine, medium or courser papers; iron-containing impurities are said to have been present in large quantities in the raw materials employed for the manufacture of low-grade papers [17-18, 29]; foxed papers were found to be more intensely and obtrusively stained after the last quarter of the eighteenth century, when the use of carbonate content diminished through the introduction of the Hollander beater that superseded the lime fermentation process, formerly used for rag pulping; according to Barrett [28], the stamper beating process and the subsequent extensive water washing had, as a side benefit, the tendency to reduce drastically the population of spore-forming microorganisms remaining in the rag after fermentation.

The MNAA museum survey

In a sampling of 1568 drawings (hand-made rag and gelatine-sized papers) was found that *ca.* 20 % was affected by foxing and the drawings of two specific periods were particularly prone to it: the first period, dating from 1560 to 1619 (59 years), where 44 % of the items presented very minute and hardly perceptive foxing stains (Figure 2); and the third period, from 1776 to 1825 (49 years), consisting of the largest sampling of drawings, with 23 % of items with a more pronounced and visually intrusive type of foxing (Figure 3, batches A-C). On the other hand, in the second and longest period, from the early seventeenth century to the late eighteenth century (155 years), only 8 % of the drawings presented staining from foxing. Although the highest percentage of foxing stains was observed on the first period, the batch size correspondingly is much smaller than the one surveyed for the third period (46 in contrast to 1039, Table 1) and the foxing pattern much

Figure 2. Discreet, very minute foxing stains in drawings from the MNAA's collection, belonging to the period from 1560 to 1619: *a)*, *b)* and *c)*, full size images (white and black scale bar size: 5 cm); *d)*, *e)* and *f)*, macro images.

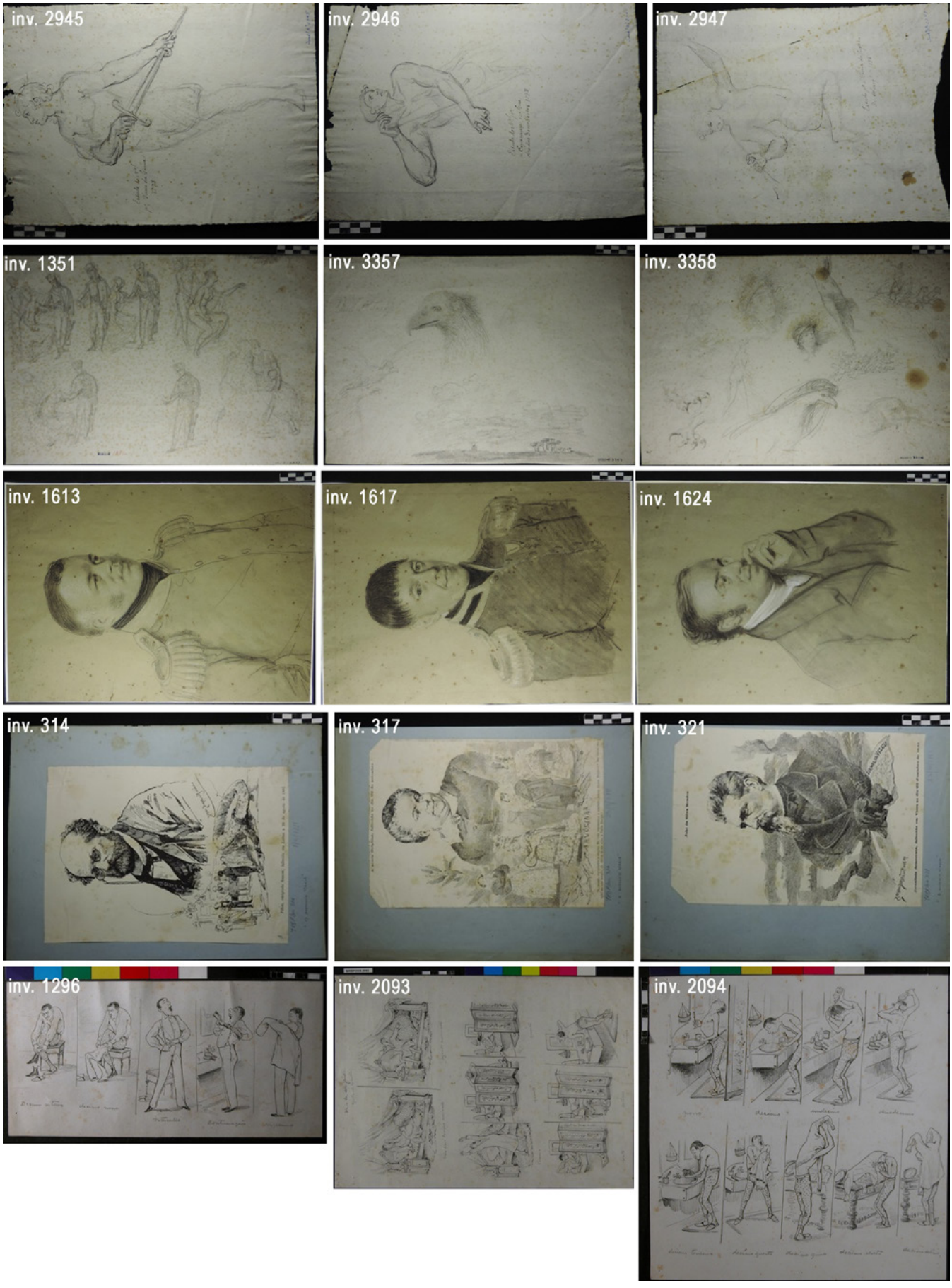

Figure 3. Reflected photographic imaging of batch A (inv. 2945, 2946, 2947), batch B (inv. 1351, 3357, 3358), batch C (inv. 1613, 1617, 1624) from the third period of the MNAA's collection (1776-1825), and batch D (inv. 314, 317, 321) and batch E (inv. 1296, 2093, 2094) from the MBP's drawing collection (black and white scale bar size: 5 cm).

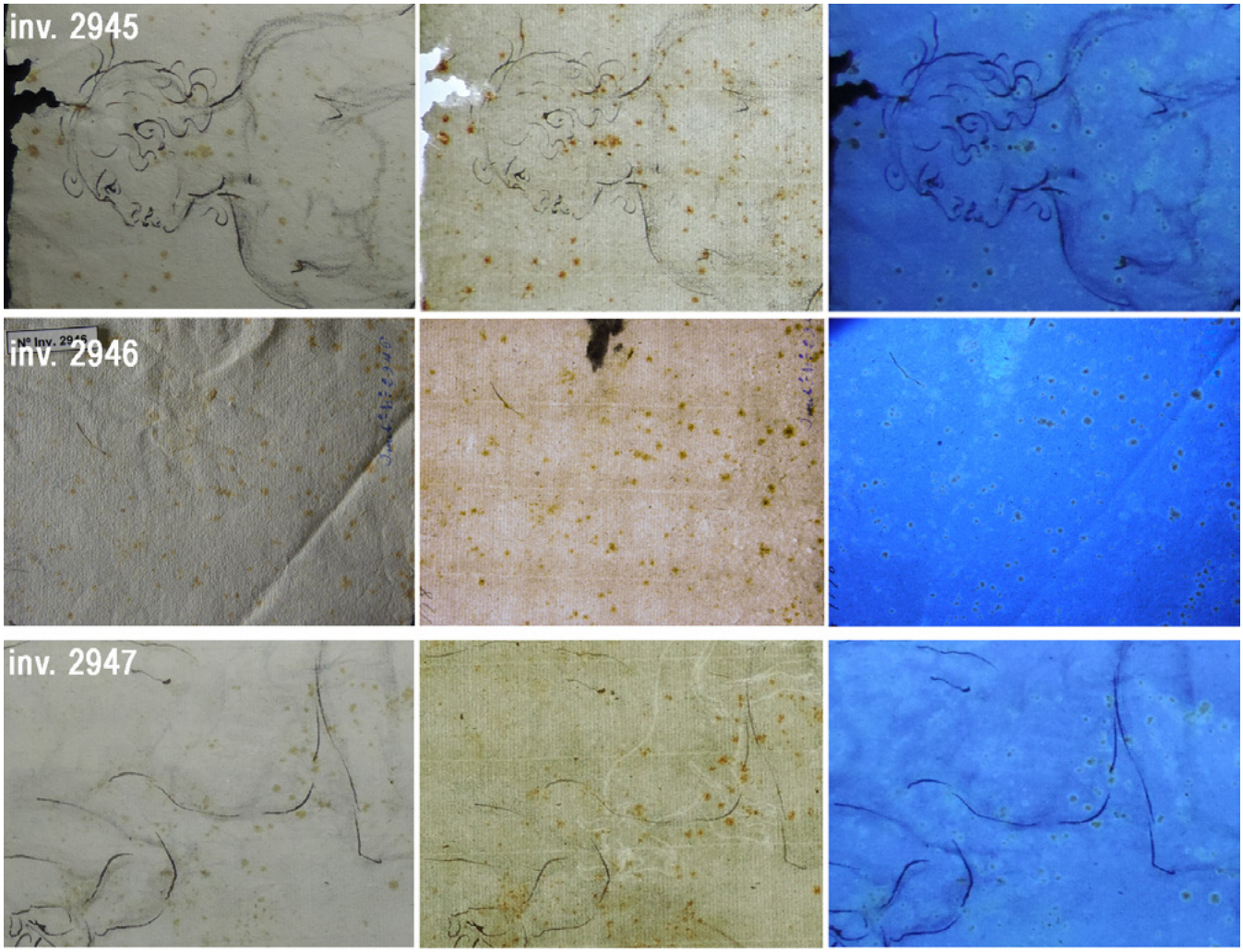

Figure 4. Macro photographic imaging of batch A. From left to right: observation under reflected light, transmitted light and UV radiation. Small orange stains with a well-defined outer contour can be observed under transmitted light while UV radiation produces a round, well-delimited white fluorescent halo surrounding a small darker centre. The halo extends beyond the visible stain.

less intrusive. Considering these two aspects, the authors admitted that the third period is, in fact, the time period where foxing had its most damaging expression.

60 % of drawings from the first period belong to A. do Vale (1550-1619) and 91 % of the foxed drawings from the third period belong to C. Wolkmar Machado (1748-1823) and A. Domingos Sequeira (1768-1837). The drawings from Domingos Sequeira mainly date from the time he lived in Portugal (1798-1926) when the Napoleonic invasions occurred and a probable scarcity of high-quality paper took place. 29 % of Sequeira's foxed papers were coloured papers, made up with coloured rags. Some of these rags probably contained iron-based mordants, which were very hard to remove even with prolonged souring [18].

The occurrence of a high percentage of foxing in the first period is possibly related to the use of gelatine sizing without potassium aluminium sulphate (PAS), as the latter only began to be regularly in use after the seventeenth century [29]. For the low percentage of foxed papers in the second period, one change could be at origin. PAS was added to the gelatine solution and the finished paper leaf continued to be dipped into the tub of a gelatine-PAS solution, which lay as a uniform and hardened film on its surface [26], making it more impervious to cycling relative humidity (RH) changes. The more visually disturbing foxing stains of the third period can probably be attributed to the alteration of the sizing process, now called engine sizing. This process incorporated the gelatine-PAS solution into the slurry of fibres and water in the Hollander beater, before the sheet was formed, permitting the oxidation of localized spots through differentiated rates of adsorption/desorption in humidity cycling [3-5]. Using surface characterization by ToF-SIMS and XPS, Benetti et al. [34] observed in a sample from the eighteenth century that the distribution of gelatine sized layer covered only in part the cellulose fibres on the paper's surface. This finding seems to corroborate the possible local oxidation at the wet/dry interface and be related to the engine sizing process that was in use by the last quarter of the eighteenth century (Figure 1). Besides, the concentration of alum in the gelatine sizing preparation was higher in the second half of the 18th century, probably due to the alteration from tub to engine sizing [26]. The increased use of PAS may

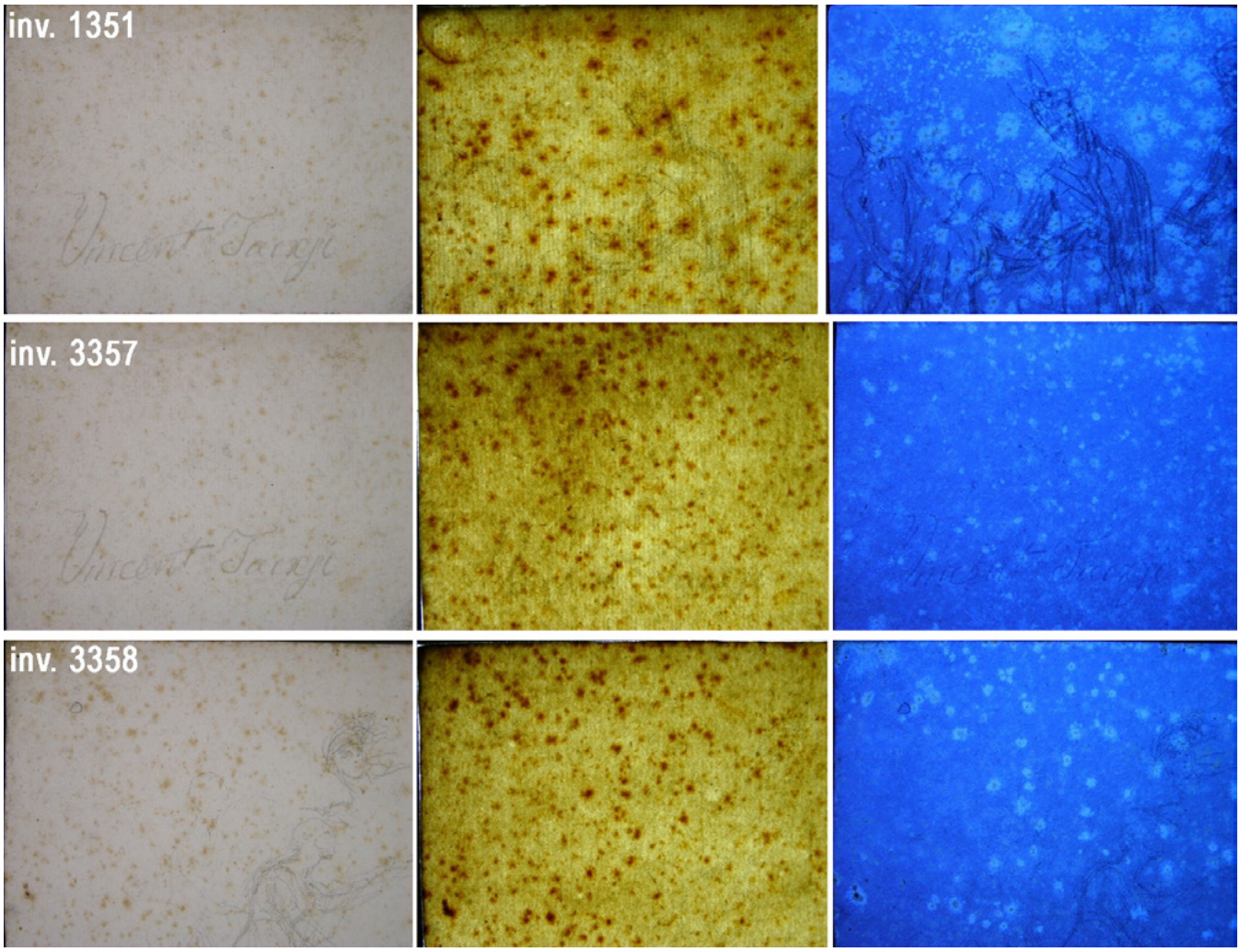

Figure 5. Macro photographic imaging of batch B. From left to right: observation under reflected light, transmitted light and UV radiation. Similar coloured foxing stains under reflected and transmitted light. Under UV radiation, drawing 1351 presents a larger white fluorescent halo surrounding the dark interior with an irregular and diffused outer contour while the halo on the stains on the other two papers is round and well-defined. Not all visible stains fluoresce.

have led to the employment of iron-contaminated alum [29], being responsible for the augment of metal impurities and decrease in carbonate content. The introduction of chlorine bleaching in the papermaking process and a broader choice of higher-quality papers after the Napoleonic wars can possibly sustain the reduction of foxing appearance in the fourth period.

The MBP museum survey

Foxing stains affect *ca.* 15 % of the 925 paper folios (621 printed folios and 304 drawings) surveyed at the MBP museum. The problem is more important in drawings than in the printed folios (20 % in contrast to 12 %; Tables 2 and 3, respectively), but for both typologies, the paper folios from the first period (1879-1885) are by far the most damaged ones.

The drawings from the first period are preliminary sketches. Being so, it is very likely that second or third-quality drawing papers were used. For this type of paper, impure gelatine-aluminium sulphate (AS) sizing, with considerable content of iron salts [18], was probably employed instead of gelatine-PAS sizing. Iron salts residues were also found in lower-quality products from mineral fillers or in caustic soda used for fibre pulping [17-18]. Nevertheless, the very large difference between the two periods considered for drawings (42 % and 16 %, respectively) cannot be exclusively attributed to technological developments. The difference in papers' characteristics could have played an important role. In fact, 77 % of the foxed papers in the first period is of a very similar white paper, while the majority of papers from the second period contain mechanical wood pulp, which is not prone to foxing [35]. Mechanical wood pulp contains lignin and this recalcitrant polymer seems to be highly resistant towards biological degradation [36]. Timár-Balázsi [37] refers that a high lignin content in a paper substrate retards microbiological deterioration due to its hydrophobic properties that hinder the penetration of water.

As to the printed folios, 23 % of the foxed folios from the first period use a blue writing paper as secondary support. Recurring to what has been reported on the use of iron-based mordants in the manufacture of coloured rags [18],

Figure 6. Macro photographic imaging of batch C. From left to right: observation under reflected light, transmitted light and UV radiation. Large brown stains which do not fluoresce. Fluorescent, scattered, white spots that resemble foxing stains are especially visible in the white chalk highlights.

this may be the case of the blue tinting of this paper. All the thin printed folios that have this secondary support are affected by foxing through contact contamination (Figure 3). The introduction of rosin-AS sizing, which began to replace gelatine-AS in the fourth decade of the nineteenth century and was in general use in the last quarter of the century [26] (Figure 1), could explain the extremely lower presence of foxing in the second period. No blue writing paper was found in this second period.

The BNP library survey

Finally, the BNP survey showed that in a sampling of 8040 folios, only a small percentage of ca. 4 % exhibited this deterioration (Table 4). In the period from 1835 to 1867, when rag fibres and gelatine size were most probably still in use [26-27], ca. 27 % of that newspaper collection was damaged, while a much lesser percentage (ca. 7 %) was found in the subsequent period, from 1871 to 1903, with the most fragile newspaper items due to the use of mechanical pulp and a very acidic rosin size. Even smaller percentages were found in the third (1907-1923) and fourth (1924-1975) periods, since the stains observed could not be considered as typical foxing, as classified by Cain and Miller [38]. These stains were probably due to the direct exposure to air in adverse RH conditions. In fact, a particular type of staining, diverse from foxing, was detected on the upper quarter of a newspaper's front page that had been folded in four for better selling distribution. Local glued paper reinforcements must have also contributed to sporadic staining.

When comparing the 1835-1867 period surveyed in the newsprint BNP collection with a similar period (1826-1850) in the MNAA drawing collection, the higher percentage of foxing (ca. 27 % in contrast to 16 %) obtained for the first collection can be attribute to the lower-quality paper used for newspapers, which would have more iron-containing impurities [18].

The periods that better coincide between the newspaper BNP collection (1871-1903) and the MBP print and drawing collections (1879-1898) show a smaller percentage of foxing in the BNP newspapers (7 % in contrast to 12.4 % and 20 %,

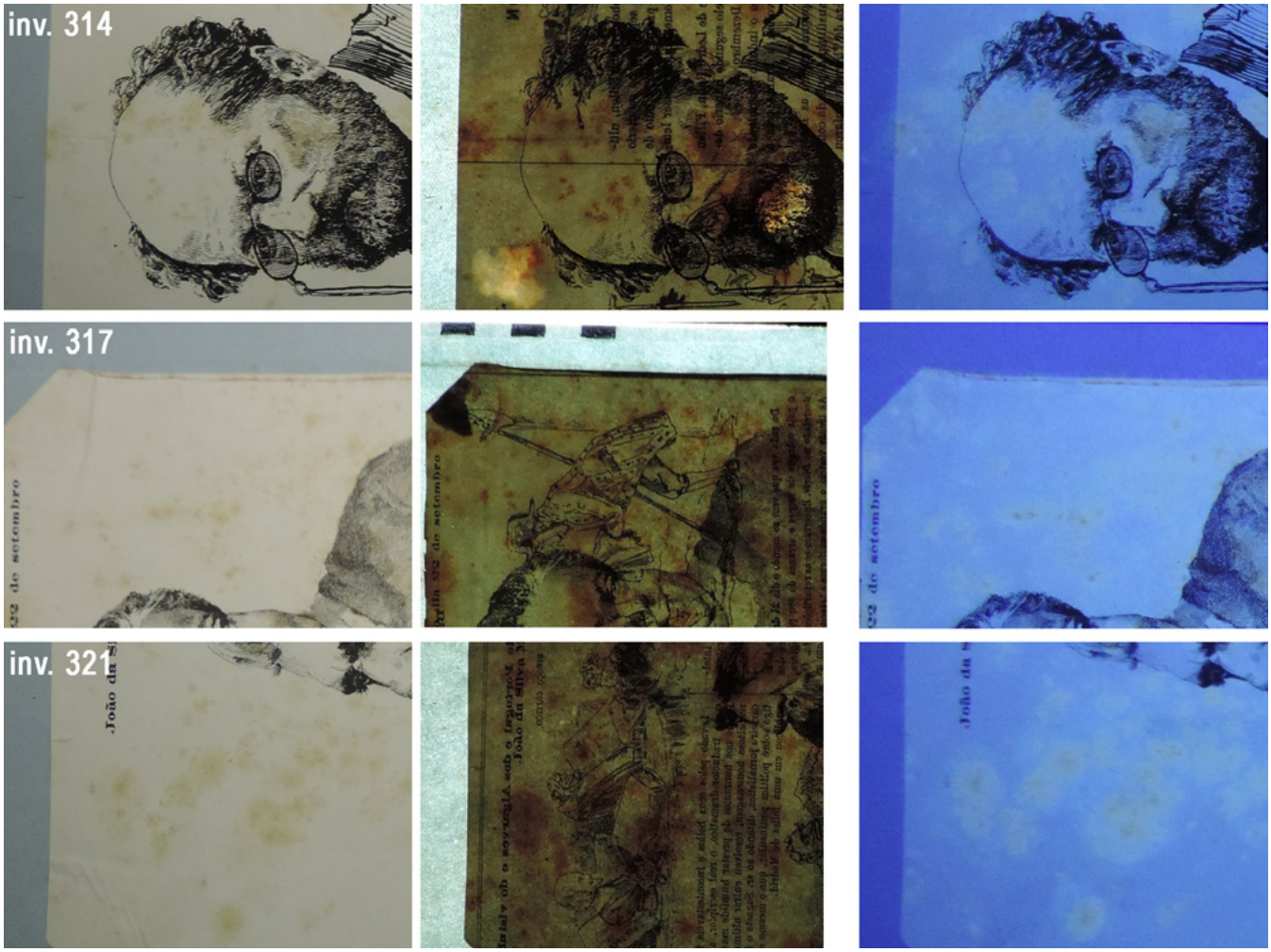

Figure 7. Macro photographic imaging of batch D. From left to right: observation under reflected light, transmitted light and UV radiation. Similar foxing stains on the three printed folios due to contact contamination with the blue secondary support, and made by light coloured, large agglomerates easily observed under reflected and transmitted light. Under UV radiation there is hardly any dark centre and the white fluorescence is much broader than the visible stain.

respectively) probably due to the use of mechanical pulp after 1883, as was detected in this survey. If we narrow down the period to 1879-1885, the foxing percentage would be 3 % for the newsprint papers (BNP) and 18.3 % and 41.5 % for the print and drawing collections (MBP). The reason for this is that mechanical pulp was first introduced in newsprinting, which used lower-quality paper. The second period of the MBP collection (1891-1898) sees foxing greatly reduced in the drawing collection (15.5 %) and hardly visible in the print collection (1.4 %) precisely due to the increased use of mechanical pulp.

Morphological characterization of selected foxing stains

The three papers in batch A, under reflected and transmitted light, have small orange stains with a well-defined outer contour that has a greasy feeling to it. Under UV radiation there is a round, well-delimited white fluorescent halo surrounding a small darker centre. The halo extends beyond the visible stain (Figure 4).

Batch B's papers present similar coloured foxing stains under reflected and transmitted light but the thicker paper, corresponding to drawing 1351, has a greater quantity of stains. Under UV radiation the white fluorescent halo surrounding the dark interior is larger and has an irregular and diffused outer contour, resembling the Cain and Miller's [38] description of snowflake stains. The other two papers' stains are very similar in tone and size and fluoresce white with a round, well-defined halo and the darker interior is very minute. Not all visible stains fluoresce (Figure 5).

Batch C's papers have large brown stains. These foxing stains do not fluoresce. Fluorescent, scattered, white spots that resemble foxing stains are especially visible in the white chalk highlights (Figure 6). These spots have not developed into stains since they were last observed in 2008 and the large foxing stains have not changed for the past 50 years, as reported by the late drawings collection's manager. The foxing stains that occur on all the white printed folios of batch D, from contact contamination with the blue secondary support, are also very similar (Figure 7). They are formed by large agglomerates that are light coloured when viewed under reflected light and especially intense under transmitted light. Under UV radiation there is hardly any dark centre and the

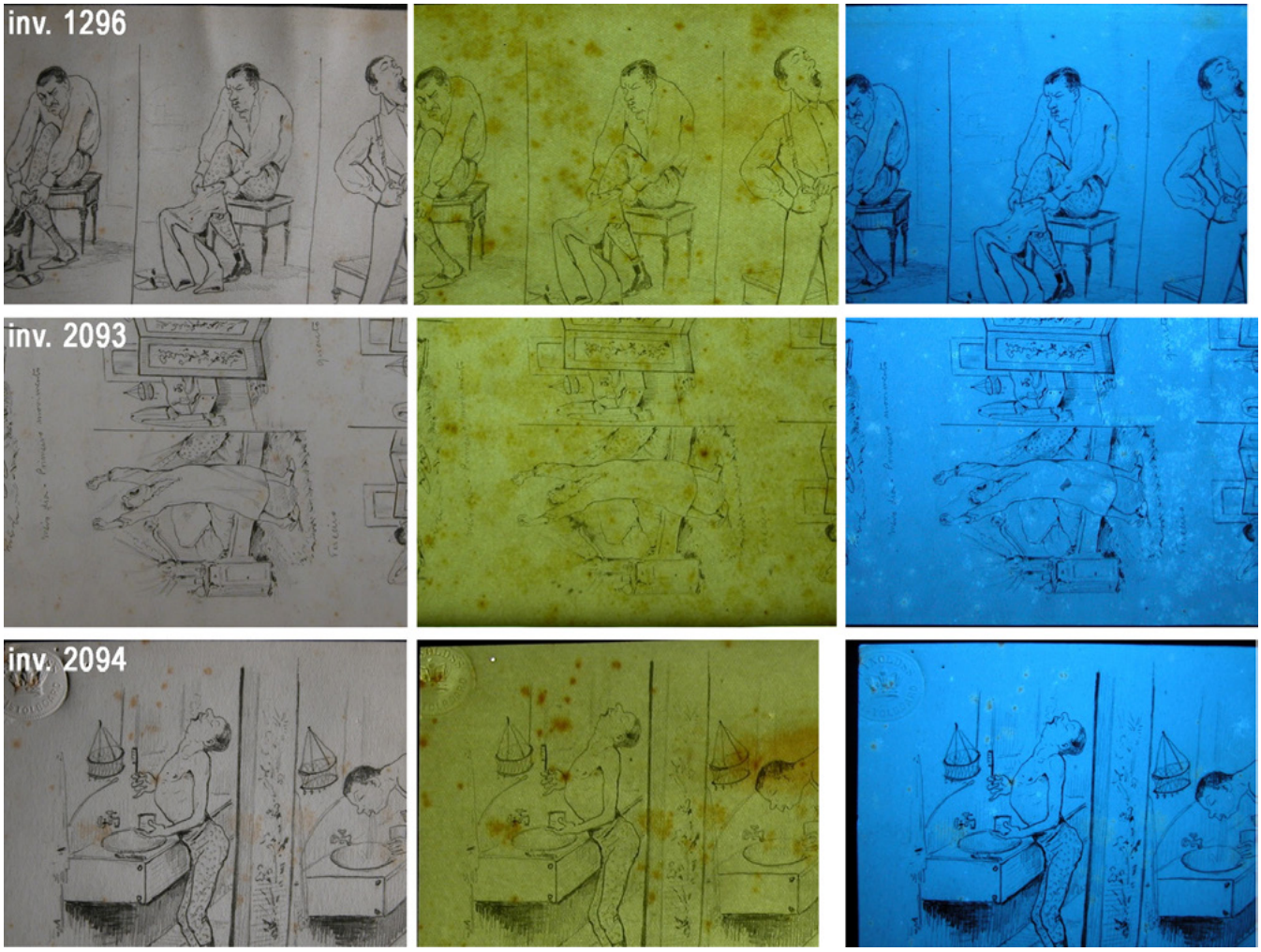

Figure 8. Macro photographic imaging of batch E. From left to right: observation under reflected light, transmitted light and UV radiation. Two types of stains can be observed: one more round and intense in transmitted light and well-delimited, and the other larger, lighter and of irregular shape. Under UV radiation the more intense and well-delimited stains do not show fluorescence but the lighter irregular shaped are all fluorescent.

white fluorescence is much broader than the visible stain. The stains in batch E are of two types: one more round and intense in transmitted light and well-delimited, and the other type, larger, lighter and of irregular shape (Figure 8). Under UV radiation the more intense and well-delimited stains do not show fluorescence but the lighter irregular shaped are all fluorescent. The stains on folio 2093, with larger and less intense colouring and irregular shape have more white fluorescent spots, especially on the right side of the image.

The detailed analysis of the images present in Figure 4 to Figure 8 seems to confirm the preliminary analysis done during the survey, pointing out that similar papers tend to develop similar foxing stains. A recent study on two gelatine-silver prints whose photographic papers present differences in composition, evidenced that the two prints accounted for a different attack by fungal and bacterial species, although nothing is said about the morphological aspects of the stains [16]. In fact, Florian [39-40], and Krstić and Schauperl [41] were convinced that foxing is a phenomenon predominantly related to the paper's specific papermaking process and raw materials.

Several foxing stains showed fluorescence if excited with UV radiation [11, 42-43]. This holds true in our UV imaging: batch images A, B, D and E showed white fluorescence in the foxing stains while only batch C did not. Fluorescence beyond visible staining has been mainly attributed to an early stage of the oxidation process of cellulose although this observation has already been questioned [24]. Recently, in a foxing conservation treatment carried out at our Laboratory, it was evidenced, through comparison between UV images before and after the treatment, that the initial fluorescence was reduced or disappeared after the washing with a slightly alkaline calcium hydroxide solution (pH 8) [25]. Valentin [44] suggested that calcium hydroxide is one of the paper conservation treatments that better reduces fungal activity. Being so, the reduction in fluorescence observed after the use of the dilute calcium hydroxide treatment may suggest the possible deactivation of microorganisms present in the foxing stains, for calcium hydroxide solution is not a reducing agent and would not be able to revert an early stage of the oxidation process of cellulose.

Conclusions

Foxing remains a subject of discussion and each published paper contributes a little more for a better holistic vision of this phenomenon.

The possibility of surveying large collections made up of different cellulosic supports and under different conditions allowed us to draw some considerations on the foxing topic: 1) photographic imaging showed that all similar papers developed similar foxing stains as was first documented by visual examination; 2) higher incidence of foxing stains observed in certain periods could be related to different papermaking technological procedures; 3) foxing seems to be more frequent when gelatine-AS sized papers were in common use than when rosin-AS sized papers were used; 4) chemical and mechanical pulps (ligneous) are more resistant to foxing than rag pulps (herbaceous); 5) a synergetic effect between three factors – the use of gelatine sizing with poorer quality and homogeneity, the presence of iron-containing impurities throughout the paper leaf and a distinct absorbency of moisture due to several factors – is, according to the authors' point of view, the major responsible for foxing incidence, being the growth of fungi within the foxing stains no more than an opportunistic act.

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