

Recipe analysis, reconstruction, and re-enactment: historical technological sources on the cleaning of easel paintings

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ABSTRACT Analysis of over 180 historical documentary sources from 1600 to 1900 covering the cleaning of oil paintings established that the use of alkalis was mentioned in over 50% of references to aqueous cleaning. Alkalis could be employed as a paste with wood ashes and water or in the form of lye. Historical alkali cleaning recipes based on wood ashes were reconstructed and characterised using titration and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Results indicate that pH depends on the wood-ash source, the age of both the ashes and the lye, as well as on the proportion of ash to water. Reconstructions of lye solutions and wood-ash pastes were applied to naturally aged model oil paints and oil paintings. Their visual impact was investigated using high resolution imaging, and chemical changes were studied with infrared spectroscopy in attenuated total reflection (ATR-FTIR) and focal-plane-array Fourier transform infrared spectroscopy (FTIR-FPA) as well as scanning electron microscopy equipped with energy-dispersive X-ray analysis (SEM-EDX). These latter investigations determined the presence of potassium within the upper layers of paint samples after exposure to wood ash lye. The potassium remained in the oil network after extensive water rinsing. This research adds information to our existing knowledge about historical cleaning methodologies and contributes to a better understanding of the current condition of paintings previously cleaned with alkalis.

Introduction

Alkaline cleaning reagents have been associated with damaged oil paint surfaces such as paint loss and “topping” of raised areas, (Burnstock and Learner 1992), and are thought to result in the saponification of the oil binder (Wolbers 2000). Similarly in historical sources, authors cautioned that alkalis could “corrode the oil of a painting” (Dossie 1758: 220) and could convert “the drying oil which binds the colours” into a kind of soap (Tingry 1804: 136).

To date no sustained systematic research has been carried out on the historical use of alkalis for cleaning oil paintings and on their impact on dried oil paint. To address this, a three-part research model was developed. First, over 180 historical documentary sources on the cleaning of paintings published between 1600 to 1900 were transcribed to a database and analysed. By organising the extracted information chronologically and by materials recommended, the central role of alkalis in aqueous-based cleaning, and a preference for wood-ash paste and wood-ash lyes, were revealed. The second

part was to determine whether damages in oil paintings, including the possible saponification of the binder, can be related to the use of these potassium-based solutions with high pH. Representative cleaning recipes were reconstructed and tested on naturally aged model oil paints and paintings. In the third part, the visual impact of the alkali-based reconstructions was recorded with high-resolution imaging and the chemical impact was investigated with infrared spectroscopy in attenuated total reflection (ATR-FTIR), focal-plane-array Fourier transform infrared spectroscopy (FTIR-FPA), and scanning electron microscopy equipped with energy-dispersive X-ray analysis (SEM-EDX).

Documentary research on historical cleaning methods (1600–1900)

The database design

References to cleaning methods and materials were collected from historical artists' manuals, books of secrets, household compendia, encyclopaedias, and books dedicated to restoration. To date, 181 sources from 1600 to 1900 have been analysed. Of these, 90% date from the 18th and 19th centuries (Fig. 1a) and 65% were published in Britain and France (Fig.1b). Over 1130 instructions were transcribed and inserted into a database.¹

To assess the popularity of specific cleaning methodologies and evidence of use, the database was designed as an 'interactive research tool' (Carlyle 2020). This involved making a series of refinements to the search fields as new information was revealed during data collection and transcription. For example: a reference to the "oldest" lye raised the question of whether the age of the lye was important. A new field to tag all records referring to the age of the lye and the age of the wood ashes used was introduced. The nature of the inquiries and the introduction of search topics grew as new records were transcribed. Previously entered data was revisited and reinterpreted continuously.

Historical cleaning methods

A chronological sort on cleaning methods (Fig. 2a) shows that aqueous methods remained current throughout the period studied. Further analyses demonstrated that the use of alkalis appeared in slightly over half of the references to aqueous methods (Fig. 2b). This finding supported the next stage of research which concentrated on the use of alkalis to clean oil paintings.

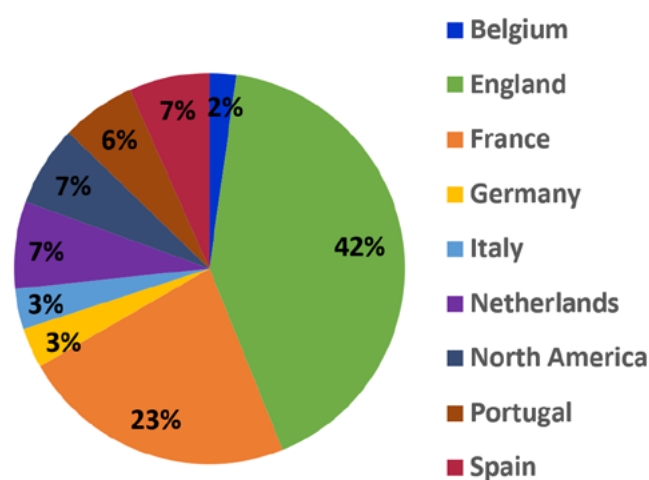
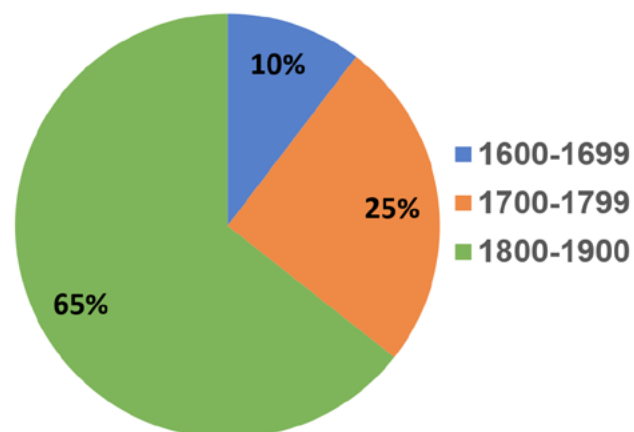


Fig. 1 (a) Historic sources by date range. (b) Sources by place of publication.

Alkali reagents employed for cleaning

Alkaline reagents were advised for the removal of surface dirt, varnish, oily layers, and stains from varnished and unvarnished paintings. While the alkaline reagents and their combinations can vary significantly, the use of lye was found to be constant over time. Historical records describe "lye" as an alkaline solution made by adding ashes, potash or soda (impure forms of potassium and sodium carbonate) to water (Richardson and Watts 1863).

Of the individual alkaline reagents used, a significant number involved the use of ashes. This is shown to be consistent over time with a decrease in the last half of the 19th century (Fig. 3a). Wood, vine lees, vine leaves and branches and woad were listed where the ash source was specified (Fig. 3b). As Fig. 3b indicates, wood was a significant source. In the sources, two ways to employ ashes to clean paintings predominate: one was to mix ashes with water and filter or decant the resulting lye,

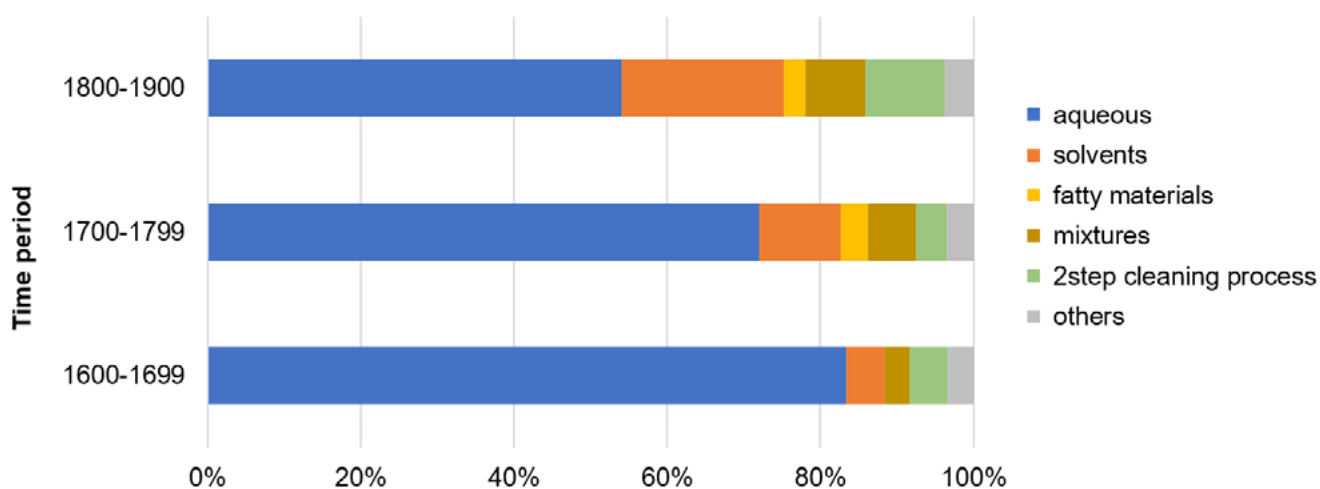
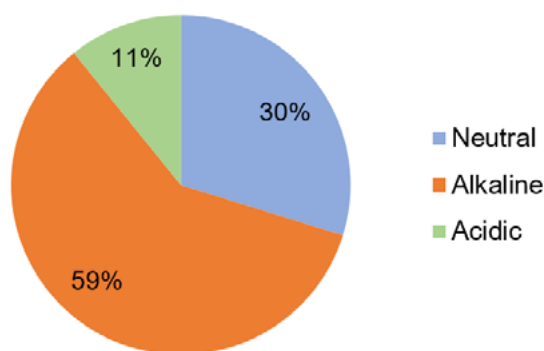


Fig. 2 (a) The main liquid cleaning methods by date range.

(b) Aqueous cleaning from 1600 to 1900.



from both woods in order to evaluate the importance of the wood type (Chomel 1725: s.v. lye).

Recipes

The proportion of ashes to water for making lye was not reported frequently. Since two recipes call for significantly different ratios, these were chosen for comparison: Robert Dossie's instructions (1758) and a recipe from *A Compendium of Colors ...* (Anon. 1808). Dossie's recipe called for evaporating off a portion of the water prior to use whereas the *Compendium's* recipe was ready to be used (Table 1).²

Age of the ashes and lye

Another variable is the age of the ingredients: Forni wrote that old ashes are always less effective (1866: 182).³ Yet in *Secrets concernans les Arts et Metiers* (Anon. 1724: 256) old lye was preferred: "Take two pints of the oldest lye..."⁴.

The preparation of ashes and lyes

Oak (*Quercus robur*) and beech (*Fagus sylvatica*) logs were burned to ashes in an open fireplace.⁵ The ashes were then passed through a 1 mm mesh stainless steel sieve to remove unburnt pieces.

A portion was stored in polypropylene (PP) zip-lock bags to reduce air exposure and another portion was left

and the other was to use the ashes and the water directly on a painting. Both methods were explored by reconstructing historical recipes.

Reconstructions

Wood choice for the ashes

Two references to the use of oak ash were found: one was by Tiquet who was a French painter, published in Holland (Tiquet 1741: 21) and Belgium (Tiquet 1741: 49–50). This was later re-worded in an anonymous publication (Anon. 1790: 108). The other was found in an anonymous publication in the Netherlands (Anon. 1772–1784: 31). A 19th-century source on lye making states that oak ashes are the strongest for this purpose (Youman 1872: 317). Because beech is mentioned in lye making recipes from the same period, albeit not for the cleaning of paintings, reconstructions were made

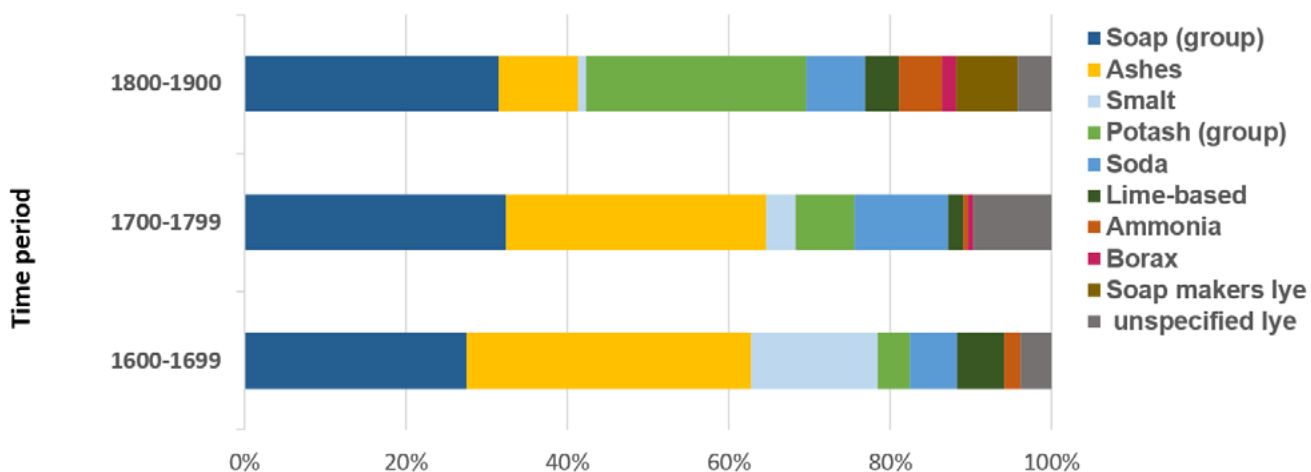
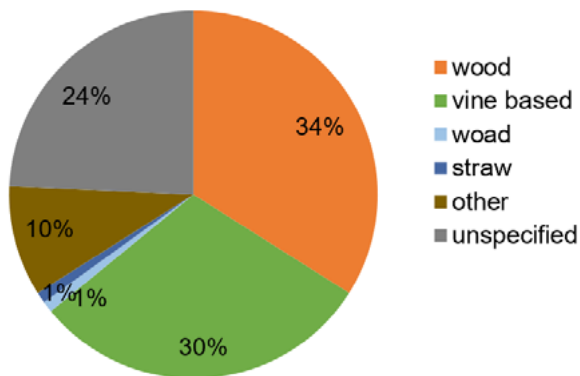


Fig. 3 (a) The individual alkaline reagents by date range. (b) Types of ashes called for in the cleaning recipes from 1600 to 1900.



mined with inductively coupled plasma atomic emission spectroscopy (ICP-AES) and scanning electron microscopy combined with energy-dispersive X-ray analysis (SEM-EDX), in order to verify the possible existence of residues in and on paintings after exposure.

Total alkalinity and pH

in the open air for 16 weeks to represent “old” ashes. The lyes were prepared by adding the ashes to ultrapure (i.e. water without ions; Millipore) water and agitating every hour for four hours.⁶ After settling, the solutions were decanted. Half the liquid made from both new and old ashes was stored in a sealed PP bottle to represent fresh lye, while the other half was left to evaporate in ambient conditions to represent old lye (Fig. 4).

Total alkalinity was established by titration using H₂SO₄ (0.1N) following a standard procedure (APHA, AWWA and WPCF 1985). The measurement of pH was performed using a glass electrode attached to a calibrated potentiometer. Table 2 reports the average values (based on duplicate titration analyses and of five pH measurements).

The pH of the freshly made lyes (which were used in the following experiments) was measured and the lyes titrated to determine their concentration of hydroxides, soluble carbonates and bicarbonates (as total alkalinity) in order to better understand their pH development over time. The elemental composition of the lyes was deter-

The variations in composition and pH of the lyes are partly explained by their different ratios of ash to water. The higher amounts of ash called for in the Dossie recipe results in a higher concentration of carbonates and bicarbonates (enhanced by evaporation). Air exposure increases the bicarbonate content due to reactions with atmospheric CO₂ (Etiégni and Campbell 1991).

Table 1 The two recipes selected for the reconstruction of wood ash lyes.

Recipe	Original units		Metric equivalent		Ratio (g/ml)		
	ashes	water	ashes (g)	water (ml)	ashes	water	
Dossie (1758: 223)	2 lbs	3 qt	907.2	2838	1	3	Needs to be evaporated
Anon. (1808: 165)	1 oz.	1 pt.	28.35	473	1	17	Ready to be used

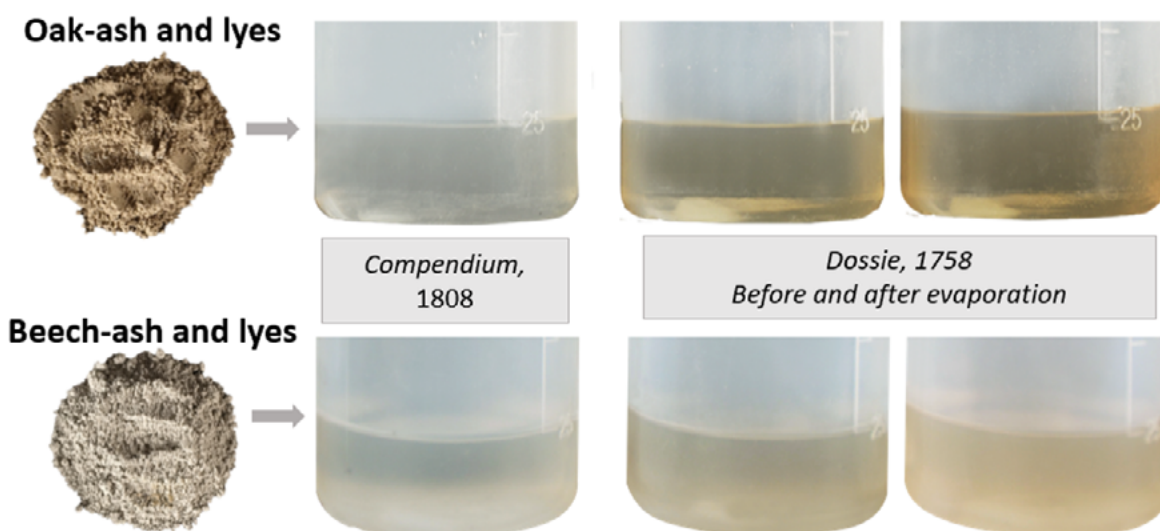


Fig. 4 Reconstruction of wood ashes and lyes, oak (top) and beech (bottom).

Higher amounts of bicarbonates results in lyes with lower pH. The use of old ashes (air exposed) also results in lower pH for the same reason.⁷

To assess the behaviour of the lyes over time, 10 ml of each new lye made with new ashes was allowed to evaporate at room temperature and the pH was followed over 14 days (Fig. 5). The presence of significant amounts of carbonates and bicarbonates and the absence of hydroxides in the Dossie lyes initially keep the pH more constant, since these compounds act as buffers. The lyes from the *Compendium* (Anon. 1808) show a faster and more marked decrease in pH as the hydroxides present rapidly react with CO₂ in the air to form new carbonates or bicarbonates.

After approximately 8–9 days, when half of the original volume had evaporated, the pH of all solutions

begins to increase slightly. As the water evaporates the solution becomes more concentrated and the equilibrium of the reactions with CO₂ changes, reversing towards the formation of more carbonates which results in the higher pH. In contrast the lyes kept in closed jars do not significantly alter in pH over time.

Based on these results the pH of the lye solutions used for cleaning in the past would vary according to the recipe used and the degree of air exposure of both the ashes and the resulting lyes.

Elemental composition

Table 3 provides an overview of the ICP-AES data for the new oak and beech ashes and lyes. The lyes were acidified with HNO₃ to a pH below 2 before elemental

Table 2 The total content in hydroxides, carbonates and bicarbonates of the reconstructed lyes. The lyes later used to assess the impact on oil paint are highlighted in grey.

Ashes		Lye	Hydroxides CaCO ₃ mg/L	Carbonates CaCO ₃ mg/L	Bicarbonates CaCO ₃ mg/L	pH
Oak	New	Dossie	0	31950	2250	11.0
		<i>Compendium</i>	50	6350	0	12.0
	Old	Dossie	0	30350	5925	10.7
		<i>Compendium</i>	0	5000	175	11.0
Beech	New	Dossie	0	85700	6425	11.1
		<i>Compendium</i>	875	8150	0	12.7
	Old	<i>Compendium</i>	0	4850	300	11.2

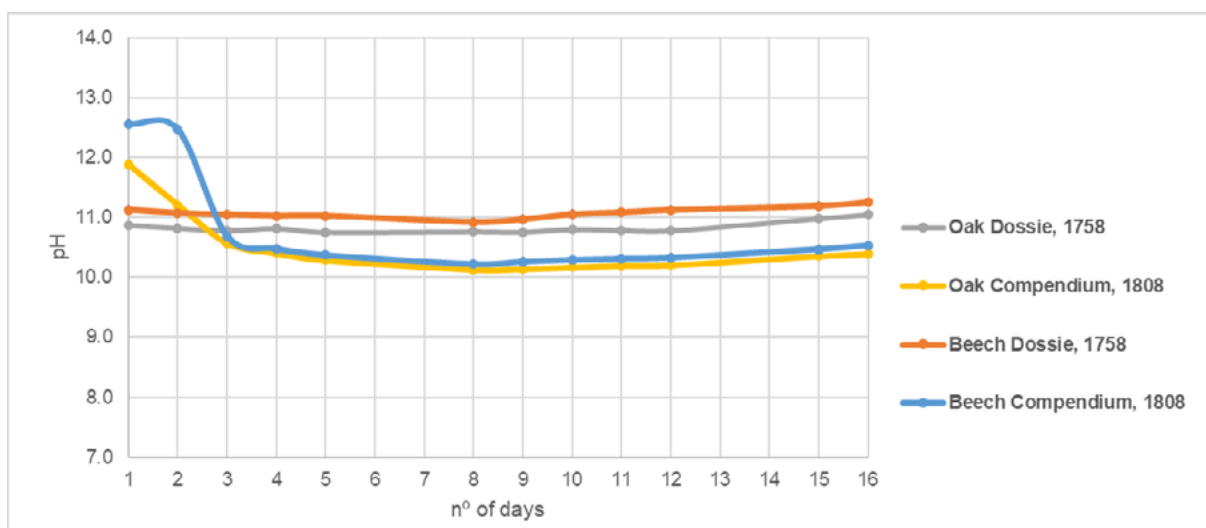


Fig. 5 The behaviour over 14 days of fresh oak and beech lyes made with new and old ashes.

quantification. The measurements reported are the average values of 3 replicate analyses.

Both oak and beech ashes are rich in calcium and potassium oxides. However, in the lyes calcium oxide is present only in trace amounts while potassium predominates. This is explained by the low solubility of calcium oxide in water (Sano *et al.* 2013). In terms of the two different recipes, Dossie's consistently shows significantly higher amounts of potassium oxide in the lyes from both oak and beech ashes. This is not surprising considering that Dossie's recipe is more concentrated to begin with and is further concentrated by evaporation before use.

Cleaning with ashes

In order to investigate the impact on oil paint of the wood-ash pastes and lyes, cleaning was re-enacted based on information in the sources.

Delivery of cleaning agents with a sponge appears frequently. Since testing materials were limited in size and availability, a natural sponge was cut into 5 by 3 cm pieces and attached with thread to a wooden stick. For comparison, small cotton swabs were also used – unlike sponges these allow a better control of variables such as size, shape and pressure on the paint surface.

Table 3 Elemental analysis of the new ashes and new lyes. The composition of the ashes is expressed in wt, % and the composition of the lyes in g/L.

Oxides	Oak			Beech		
	ashes	Dossie's lye	Compendium lye	ashes	Dossie's lye	Compendium lye
CaO	41.7	0.028	0.031	35.3	0.009	0.004
K ₂ O	18.6	30.9	9.0	18.4	76.5	9.0
P ₂ O ₅	4.1	0.017	0.014	3.2	0.10	0.005
MgO	3.0	0.11	0.020	6.1	0.07	0.019
SO ₃	2.1	3.06	0.41	1.6	2.99	0.35
ZnO	0.82	0.00002	0.00001	0.25	< 1.9x10 ⁻⁶	0.003
SiO ₂	0.20	0.031	0.012	0.28	0.022	0.013
MnO	0.23	0.00003	0.00003	0.03	< 1.2x10 ⁻⁶	< 1.2x10 ⁻⁶
Fe ₂ O ₃	0.16	0.00002	0.00001	0.12	0.00003	0.0001
Al ₂ O ₃	0.12	0.00007	0.0001	0.11	0.0001	0.0001
Na ₂ O	0.07	0.069	0.019	0.03	0.023	0.008

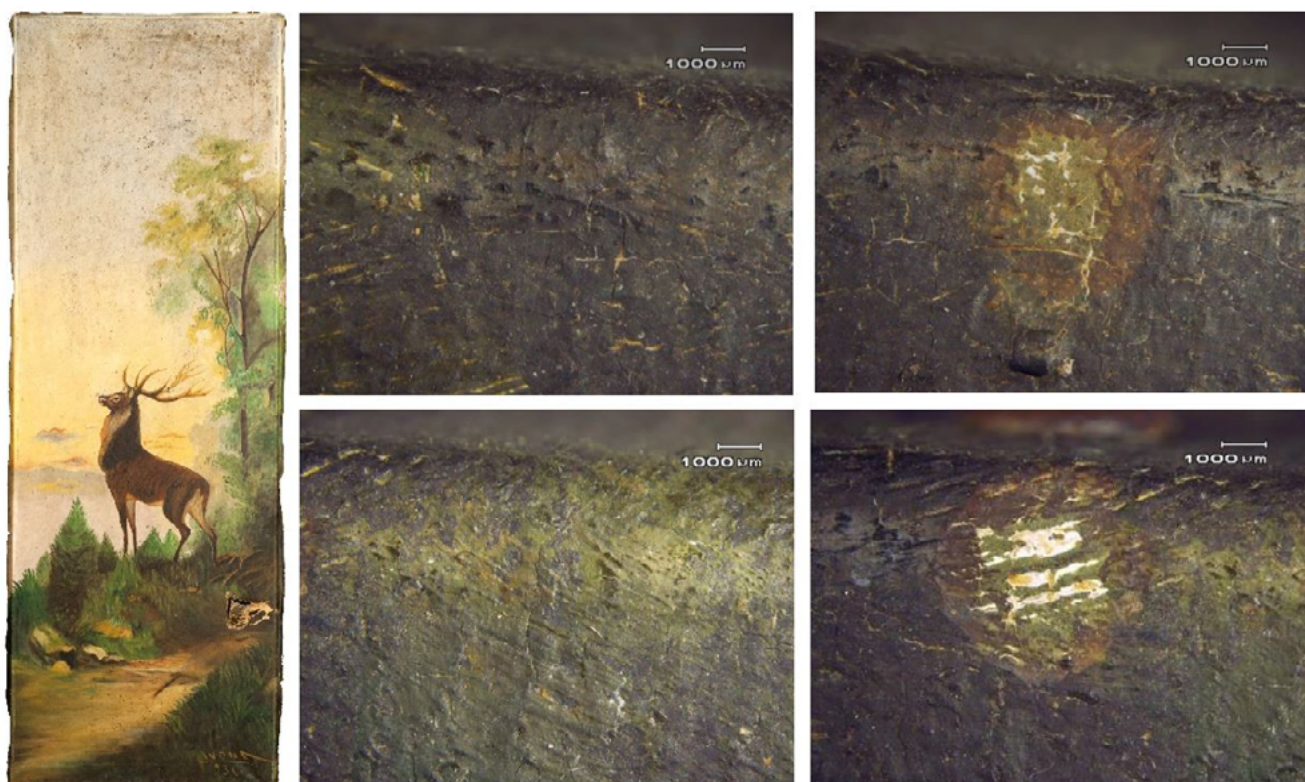


Fig. 6 Overall view and details of the surface of an early 20th century oil painting with a natural varnish after cleaning tests with (a) water, (b) ethanol, (c) Dossie's oak-ash lye and (d) the same oak ash as paste.

The effects of water, ethanol, oak-ash paste and Dossie's oak-ash lye were tested on an early 20th century oil painting with a natural varnish. The cleaning agents were applied with repeated swabbing for 20 seconds. No visible changes were apparent with Millipore water alone and with 100% ethanol, however the application of oak-ash paste and lye resulted in paint losses in keeping with the pattern of damages seen on old paintings, often referred to as abrasion (Fig. 6).⁸

The chemical impact of wood ash lyes

Naturally aged, highly characterised oil paint reconstructions prepared in 1999 (MOLART) and 2004 (HART) and applied to Melinex® (Carlyle 2001a; 2005) were used to evaluate the chemical impact of the lyes. Four hand-ground paints in linseed oil were selected with the following pigments (detailed in the Appendix):

- Umber (MOLART, made in 1999)
- Reconstruction of traditional stack process lead white in oil (HART, made in 2004)
- Vine black (MOLART, made in 1999)
- Modern lead white in oil (MOLART, made 1999)

A drop of 10 μm of lye was applied to the paint surface for 10 seconds or 60 seconds. Two reconstructed lyes were selected (Table 2), namely, Dossie's lye (1758), with pH 11 and the recipe in the *Compendium* (Anon. 1802) with pH 12.0. Tests were also made with a diluted lye (1 ml of Dossie's lye to 500 ml water) which still exhibited high alkalinity (pH 10.5).

Millipore water (pH \sim 6.2) and 100% ethanol were also included for comparison. Test areas were either left without rinsing (since this was not always specified) or rinsed with a drop of Millipore water. *In situ* ATR-FT-IR was used to assess the molecular composition of the paint surfaces before and after treatment. Exposure to water and ethanol did not reveal significant chemical alterations detectable with this technique. Fig. 7 shows the ATR-FTIR spectra from the umber oil paint before and after 60 seconds of cleaning with Dossie's lye followed by water rinsing. Exposure led to a decrease in the relative intensity of the carbonyl stretching bands of the esters and acids (C=O) from the oil binder at \sim 1735 cm^{-1} . The appearance of a more pronounced band at \sim 1560 cm^{-1} is attributed to the formation of carboxylates (COO⁻). The frequency of this asymmetric stretching band indicates the presence of potassium soaps (Spring *et al.* 2005). These two features were also observed in all of the paint reconstructions after exposure to both the Dossie and *Compendium* lyes.

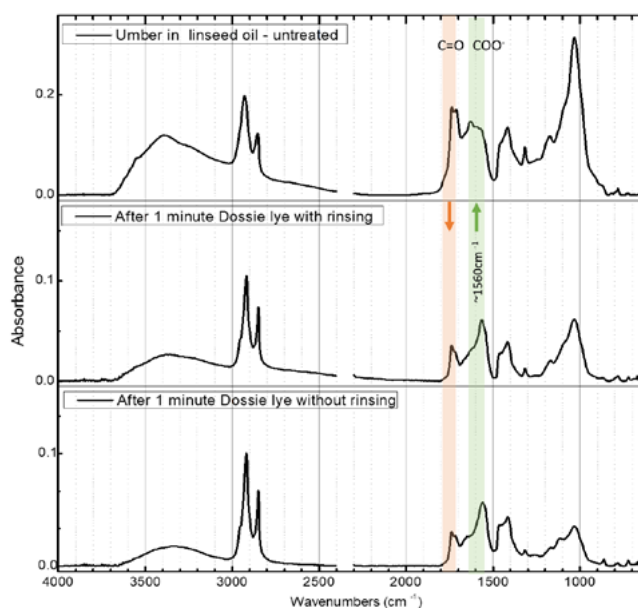


Fig. 7 ATR-FTIR-spectra of the umber oil paint (MOLART, made in 1999) before and after 60 seconds exposure to Dossie's oak ash lye (pH 11) with and without rinsing.

Repeated and prolonged water-rinsing on the vine black and stack-process lead white paints did not change the band at $\sim 1560\text{ cm}^{-1}$, demonstrating that once formed, the potassium soaps remain in the linseed oil network.⁹ The effect of a shorter contact time between the lye and the paint surface was investigated using the stack process lead white oil paint sample (HART, made in 2004) (Fig. 8). Similar results were obtained even when the exposure time was lowered to 10 seconds, i.e. there is a decrease in the carbonyl stretch band at 1735 cm^{-1} and an increase in the band assigned to carboxylates, at 1565 cm^{-1} .

Tests with the diluted lye (on samples of vine black and both lead whites) did not result in a detectable increase of the band at $\sim 1560\text{ cm}^{-1}$. The diluted lye did not contain a significant concentration of potassium (0.08 g/L versus 30.9 g/L in the undiluted solution).

FTIR-FPA was used to map carboxylates in a cross-section from the stack process lead white oil paint (HART, made in 2004). The middle image in Fig. 9 shows a false-colour image of the cross-section of the paint after 60 seconds of exposure to Dossie's lye followed by rinsing. A high concentration of carboxylates was detected at the top region of the sample (around 10–50 μm).

SEM-EDX mapping of two cross-sections from the stack-process lead white paint are shown in Fig. 10. In the top row the paint had not been exposed to lye, whereas the cross-section shown in the bottom row is from an area exposed to lye followed by water rinsing.

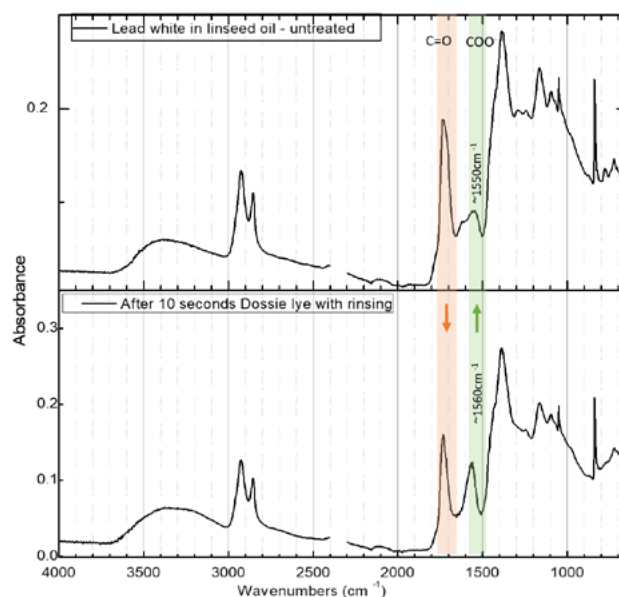


Fig. 8 ATR-FTIR-spectra of a lead white oil paint sample (HART, made in 2004) before and after 10 seconds exposure to Dossie's oak ash lye (pH 11) followed by rinsing.

As can be seen, the paint did not originally contain potassium. However, in the sample exposed to lye followed by water rinsing, potassium can clearly be detected in the top region of the sample.¹⁰

Conclusions

The analysis of a large collection of documentary sources established that alkalis have been recommended for cleaning paintings for centuries, and that wood-ash paste and wood-ash lyes could be considered representative of a class of alkaline cleaning agents used in the past.

The recipe reconstructions proved to be highly valuable for exploring variables in pH related to the use of different wood sources and to different exposure times of ashes and lyes to air, demonstrating that the pH could reach very high levels. Even after significant dilution (1 ml to 500 ml water) the reconstructed lye had a pH of 10.5.

The highly characterised oil paint reconstructions from the HART and MOLART projects proved valuable for exploring the chemical impact of alkali-based cleaning agents, albeit on relatively fresh oil paint (16 to 21 years of natural aging). The ATR-FTIR results indicate that potassium soaps are formed as a result of lye exposure, and EDX mapping demonstrates that potassium residues remain in these paints even after water rinsing.

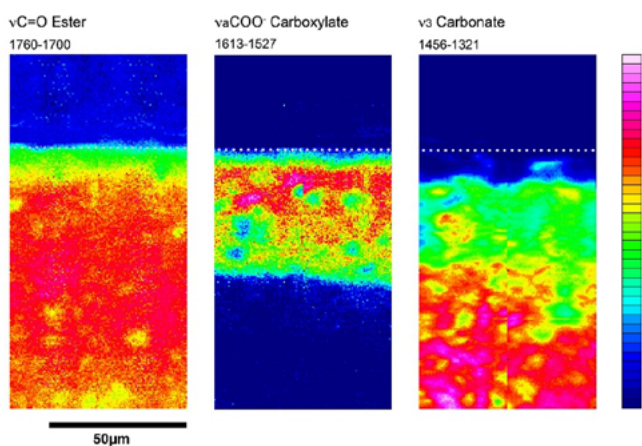


Fig. 9 FTIR-FPA of the stack process lead white oil paint (HART, made in 2004) show the relative intensity of the IR signals. The integrated spectral ranges are given above each. The ester band ($1760\text{--}1700\text{ cm}^{-1}$) on the left shows the distribution of oil. In the centre image, the carboxylate band ($1613\text{--}1527\text{ cm}^{-1}$) is more intense (red areas) in the top region of the cross-section. This indicates saponified paint (due to lye exposure). Exposure also affects the carbonates ($1456\text{--}1321\text{ cm}^{-1}$) in the lead white pigment ($2\text{PbCO}_3\cdot\text{Pb}(\text{OH})_2$); as the right image shows a lower intensity of this band on the top part of the sample.

The persistence of potassium residues after water rinsing in the experimental conditions requires further investigation to establish whether this occurs in historical oil paintings. If so, the next step would be to evaluate whether previous exposure to alkalis can leave oil paintings more vulnerable to aqueous solutions in future cleaning or even from exposure to environments with high humidity.

Increased knowledge about previous cleaning campaigns can lead to a better understanding of the current condition of a painting and help to tailor treatment options, especially for cleaning.

Acknowledgments

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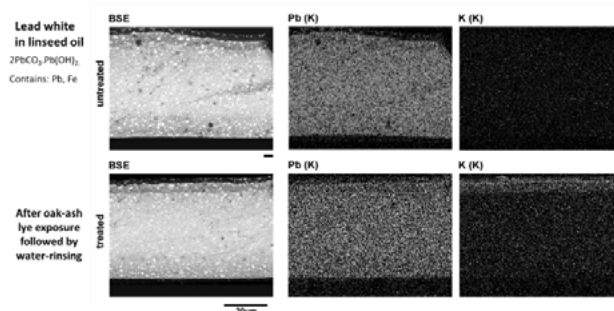


Fig. 10 EDX mapping of two samples from a lead white in linseed oil (HART, made in 2004), untreated (top row) and after exposure to Dossie's oak ash lye (pH 11) followed by rinsing (bottom row).

Notes

1. An early version of the database was developed by Stols-Witlox (2011) and was supplemented with 19th-century British recipes collected by Carlyle. The database has been redesigned and further populated by Devesa using FileMaker® pro 12.
2. The original units for the reconstructed recipes were converted to an equivalent metric system using the conversion tables for *Currency, Weights and Measures* supplied in Carlyle (2001b: 545–6).
3. *Le ceneri nuove de' nostri focolari sono da preferirsi alle vecchie, le quali riescono sempre meno efficaci.*
4. *Prenez deux pintes de la plus vieille lessive...*
5. Wood logs were harvested from forests in the Dutch province of Utrecht in the Netherlands.
6. For the lye reconstructions, ultrapure (Millipore) water and polypropylene containers and tools were used to avoid contaminants. The water used in the reconstructions was purified using MilliQ water generation equipment. From here on the term Millipore is used for the deionised water.
7. These results are in keeping with research by Demeyer *et al.* (2001) which concluded that alkalinity decreases with the time of storage of the ashes.
8. Dossie (1758: 225) implied that ash paste would be abrasive, however the reconstructed ashes felt very soft to the touch. They did however obscure the surface during use, so that damage would only become visible after water rinsing. This inconvenience had already been reported by Forni (1866: 73). It was also difficult to limit the application of wood-ash paste to a small area, especially when using a sponge.

9. Potassium soaps remain in the paint because the acid groups in the negatively charged stationary phase in the paint prevent washing out of the potassium ions. This is serendipitous evidence for the presence of a negatively charged cross-linked network in oil paint. It is also indirect proof that the positive charges of metals like lead play a central role in the stabilization of aged oil paint.
10. The darker band at or near the surface of both samples (left side images) represents an oil-rich band frequently found in HART and MOLART reconstructions of single layers of oil paint made with lead-based pigments and linseed oil. It is interesting to see that the potassium concentration coincides with this oil-rich area and does not appear to have penetrated deeper into the paint body. This interaction of the lye with oil where it has concentrated near the surface now raises the question of whether potassium will be detected in more homogenous oil paint where this concentration of oil binder does not occur.

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Second Edition, lately printed at Paris, in two Volumes, Folio, written by M. Chomel: With considerable alterations and improvements. Revised and Recommended by Mr. R. Bradlev Professor of Botany in the University of Cambridge, and F.R.S. In Two volumes. Vol. II I to Z. London: Printed for D. Midwinter, at the Three Crowns in St. Paul's Church-Yard.

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Appendix**Information taken from the MOLART (Carlyle, 2001) and HART (Carlyle, 2005) reports.**

Project	Sample	Code	Date Prepared	Pigment	Pigment (g)	Oil	Oil (g)	Percent oil by weight	Support
MOLART	Umber	XU	18.11.99	Kremer Umber Pigment. #40710 Umbra gebrannt cyprisch bräunlich	8	Water-washed Linseed Oil (prepared 1999 from Electra Linseeds purchased 1999)	8	48.1	Melinex®
	Lead white	XD	16.11.99	Dutch Process lead White (Loodwit Schoonhoven de Kat)	25		6.43	19.3	
	Vine black	XB	25.11.98	Kremer Black Pigment. : #47000 *Rebschwarz reines Pflanzenschwarz, dt.	8.1		6.1	41.3	
HART	Lead white	RM S2.18 SUWLOWE	09.12.04	Seynaeve unwashed stack process lead white	100.5	Water washed Linseed oil (prepared Aug-Nov 2004 from MOLART 1999 Seeds)	14	12.2	