Historical recipes for preparatory layers for oil paintings in manuals, manuscripts and handbooks in North West Europe, 1550-1900: analysis and reconstructions

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Figure 14.1  Grinding lead white in demineralised water on a granite slab with a glass muller
Chapter 14 ‘To prepare white excellent⋯’.
Reconstructions investigating the influence of washing, grinding and decanting of stack-process lead white on pigment composition and particle size

Of this colour there are two sorts at the colour-shop, the one called ceruss, which is the most pure and clean part; the other is called by the plain name of white-lead.

John Smith 1753

14.1 Introduction

Chapter 13 proposes that lead white processing by washing is a stage that may not have received equal attention in lower quality pigments. Chapter 13 also quotes a number of recipes that show that lower quality whites may have been employed in preparatory layers. The present chapter investigates the influence of a number of processing methods involving water and vinegar on lead white quality and attempts to determine if the omission of these refinement steps has an effect on the stability of (preparatory) layers that contain lead white.

The present study is a further exploration of the effects of lead white washing. A first step in examining the question whether lead white quality influences the degradation defects of the pigment in oil paint was taken in earlier research by the HART Project team, led by Carlyle. This earlier project investigated the effect on water washing on the presence of lead acetate in the lead white, as historical sources complain about the presence of lead acetate in lead white and link its presence to the occurrence of degradation phenomena. Reconstructions executed for the HART Project demonstrate that lead acetate is indeed removed by water washing. Reconstructions allowed Carlyle to conclude that washed and non-washed lead white paints have different flow properties, and that paint made with the unwashed pigment has a more yellowish tinge.

1 Smith 1753: 15-6
2 This paper is a modified version of: Stols-Witlox, Megens, and Carlyle 2012.
3 The HART Project was a project inside the De Mayerne Programme, a Dutch multi-disciplinary research project sponsored by NWO (Dutch organization for Scientific Research) that ran between 2002 and 2005. The HART Project was headed by Dr. Carlyle and focused on Historically Accurate Reconstruction Techniques. See HART project report Carlyle 2005 (unpublished), Carlyle 2006.
4 See Carlyle 2005 (unpublished): Chapter 2 and Carlyle 2006. Examination of artificially aged lead white and oil paints do not show a link between washing and the disruptions in the paint samples that could be caused by the formation of lead soaps. However the paints were still relatively fresh when examined.
As has been explored in Chapter 3, besides adulteration with cheaper pigments, lead white quality can be influenced by several other factors: not only is the purity of the raw ingredients considered to be important, but also the reaction (or corrosion) conditions as well as later processes such as washing, grinding and decanting of the pigment. While most painters would not have been able to influence reaction parameters, as the pigment was probably often produced outside of their studios, they were in a position to select lead white with particular visual characteristics and they would have had the possibility to further process lead white themselves and thereby influence its quality. The fact that large numbers of surviving recipes for artists provide instructions for washing and grinding lead white suggests that such processing treatments may have been common (see Appendix 21, Tables 14.1-3). This information is highly relevant, because paintings provide evidence of the use of different qualities of lead white.

When evaluating preparatory layers, knowledge of the influence of pigment refinement methods on a pigment’s chemical composition is important, since the state of the pigment, either refined, unrefined or partially refined could result in a pigment with a different chemical reactivity or particle size ranges.

Lead white is usually referred to as basic lead carbonate, but Olby (1966) showed that it is a mixture of cerussite (PbCO$_3$) and hydrocerussite (2PbCO$_3$.Pb(OH)$_2$); other lead salts like plumbonacrite (Pb$_5$O(OH)$_2$(CO$_3$)$_3$) may also be found on occasion. Cerussite and hydrocerussite are in chemical equilibrium, which means that depending on the circumstances, they can be converted into each other. Therefore the presence and ratio of lead salts in a given pigment sample will depend on variables during the production process - such as the location of the ceramic container within the stack itself, the quality of the starting materials - or on processing methods. Some reports in the late nineteenth and early twentieth century state that the freshly produced pigment contained some residual lead acetate.

Most studies have confirmed the presence of lead white in paintings by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Although this method detects the presence of the element lead, it does not identify the formulation or quantity of lead salts present in the pigment. Therefore little information on the exact composition of lead whites in paintings is available in the modern technical literature. However, the SEM can provide additional information on lead white. Since SEM backscattered-electron images show particle morphology, they may be used to obtain an indication of whether or not lead white has been post-processed.

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5 Plumbonacrite is reported to transform easily to hydrocerussite and is not always detected in lead white samples (Olby 1966: 2509-2512). Its presence was identified with XRD by Hallebeek of the (then) Netherlands Institute for Cultural Heritage in lead white samples analysed for the HART Project (Carlyle 2006: 50).
8 Carlyle 2006: 15.
This approach was successfully employed in a recent study by Boon and Oberthaler (2010) of The art of painting by Johannes Vermeer, dated 1668. SEM backscattered-electron images demonstrated that the top layers of whitish passages in the painting contain a lead white with very small particles (possibly denoting a very fine grade of pigment), whereas for the ground and lower paint layers, a much coarser lead white had been employed with a much larger range of particle or aggregate sizes (see Fig. 14.2). Berrie & Matthew (2011) and Albrecht (2012) have reported similar differences in particle size.

How were different grades of lead white obtained, what was their exact composition and what are the possible consequences of the use — or lack of use — of processing methods for the visual characteristics of paint layers and for the way the paint ages? The present chapter investigates the effects of washing, grinding and decanting methods by reconstructing historical recipes, and analysing the effects of these treatments on pigment morphology and composition.

### 14.2 Materials and methods

Recipes analysed for the present study include those that concern both lead white processing in professional manufacturing practice and recipes intended primarily for artists (see Figs. 13.5a and b). The majority of lead white processing recipes, especially those describing professional manufacturing methods, mention washing or grinding with water. The second largest group consists of instructions for grinding or washing with vinegar, vinegar being mentioned mainly in recipes intended for artists (see Chapter 13).

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9 Boon and Oberthaler 2010.
10 Argon ion polishing of lead white oil paint cross-sections (Boon and van der Horst 2008), followed by ultra high magnification with SEM demonstrates that so-called large ‘particles’ of lead white are not solid material but are composed of aggregates of small particles.
Because of their relative frequency, these two methods were selected for comparative reconstructions. Reconstructions were executed with traditionally prepared stack process lead white,\textsuperscript{12} thoroughly washed with distilled water.\textsuperscript{13} Vinegar for grinding with the lead white was prepared from organic, sulphite-free red wine and vinegar culture (bacteria).\textsuperscript{14} Lead white pigments, which have been further processed by grinding with vinegar, and/or further water washing, were subsequently made into oil paint by hand-grinding on a granite grinding stone using poppy oil extracted from a single seed lot from a single supplier.\textsuperscript{15} The paints were spread on polyester film (Melinex) with a hogshair brush and with a drawdown bar. All dry pigments produced were analysed with X-ray diffraction (XRD),\textsuperscript{16} and the oil paints were then analysed in cross-section with SEM-EDX.\textsuperscript{17} Colour measurements were made on the paint films using a Konica-Minolta spectrophotometer.\textsuperscript{18}

### 14.3 Water washing

A particularly detailed description of how to wash lead white is provided in a recipe titled ‘To prepare white excellent’, recorded by Daniel King (1653–7):

> Take a good quantity of Seruse, and being grosly braised put it into a fine earthen bason or great China dish then put it to a good quantity of running water wherein wash the Ceruse till it be thoroughly mixed with water. Then let it settle 2 or 3 hours which done, tast the water and you shall find it tast harsh and unpleasant. Observe well the tast and poure the water off and cast it away. You shall find this water to carry away with it a deale of grease rising on the top. Then add to as much more water, and then stirre the ceruse as before and tasting it poure off the cleare water reserving the bottome. This work you must reiterate some dozen times or more till by continuall washing you find your water hath washt away all the salt out of the Ceruse.\textsuperscript{19}

\textsuperscript{12} Produced by Jef Seynaeve, Belgium, for the HART Project.
\textsuperscript{13} Distilled water was added to previously crushed lead white. Pigment and water were stirred for 2 minutes. After settling of the pigment, supernatant water was poured off and replaced with fresh distilled water 8–10 times. This method closely follows the one used by the HART Project. (Carlyle 2006: 25–26).
\textsuperscript{14} 50 mls of vinegar culture (Broumland of Everlo, Belgium, purchased 18/9/2010) were added to 500 mls sulphite-free organic red wine (Stellar Organics, Shiraz, South Africa. Imported: Coenecoop Wine Traders B.V., 2742 RC Waddinxveen). The liquid was allowed to acidify during 4 weeks in a cool, dark place. The resulting vinegar had a slightly pink colour and a pH of 3–4 (Macherey-Nagel pH-Fix 0–14).
\textsuperscript{15} Poppy oil produced by the HART Project, see Carlyle (2006) for details.
\textsuperscript{16} The crystalline phases were analyzed by X-ray Diffraction (XRD) using a Discover D8 microdiffractometer with a general area detection diffraction system (GADDS) two dimensional detector (Bruker AXS, Karlsruhe, Germany). Powdered samples were applied in a little cedar oil on a Silicon zero diffraction plate. Diffractograms were acquired in reflection mode with CuKα radiation (40 kV, 30 mA). The GADDS software was used for integration and the Bruker AXS Eva software for phase identification using the PDF database.
\textsuperscript{17} JEOL 5910LV with thermo scientific energy dispersive X-ray spectrometry system with Noran System Six software.
\textsuperscript{18} Konica Minolta CM-2600d spectrophotometer, white calibration 7004450.
\textsuperscript{19} King 1653-7: 38-9.
The salt mentioned by King most probably consisted of lead acetate. During water washing of lead white carried out by the HART Project, lead acetate levels were monitored; after numerous water changes lead acetate was no longer detectable.\textsuperscript{20} An overview of water washing recipes within the period under investigation (Appendix 21, Table 14.1) shows that the main methods used were either washing with large amounts of clean water, repeated grinding with water on the slab (Fig. 14.1) or a combination of both treatments. Comparison of XRD analyses of unwashed and water-washed lead white confirms the findings of the HART project: lead acetate is indeed removed from lead white by repeated washing.\textsuperscript{21} Furthermore, these reconstructions show a shift in the balance between cerussite and hydrocerussite, with the washed lead white containing less hydrocerussite.

### 14.4 Vinegar grinding

As noted above, besides water washing, artists were regularly advised to grind or wash lead white with vinegar before use. Recipes generally specified thorough water washing afterwards to remove all traces of this acid. Some recipes described how the lead white would discolor and become black during vinegar grinding. This blackening would disappear after washing with water. Several recipes mentioned heating lead white with vinegar as a refining method. Barrow (1735) stated that rectified vinegar caused

![Diffractogram with unwashed (black), water washed (blue) and vinegar washed (red) lead white](image)

\textit{Fig. 14.3 Diffractogram with unwashed (black), water washed (blue) and vinegar washed (red) lead white}

The position of cerussite peaks is indicated with blue vertical lines, the position of hydrocerussite peaks is indicated with red vertical lines. An increase in cerussite proportion is clearly visible in, for instance, the 25.4 position.

\textit{Diffractogram © Luc Megens, RCE}

\textsuperscript{20} Carlyle (2006). Analysis performed by Katrien Keune.

\textsuperscript{21} Carlyle 2006: 25–6.
‘fermentation’ of the lead white (presumably the formation of gas bubbles). Appendix 21, Table 14.2 provides an overview of recipes for washing with vinegar that were published within the period under investigation. Although the number of recipes prescribing vinegar washing is lower than those for water washing, it is evident that vinegar is mentioned frequently throughout the period under investigation.

A series of grinding experiments following the instructions of Le Pileur d’Apligny was executed with unrefined stack-process lead white and vinegar. Dry, unwashed pigment as supplied from the maker, was transferred to the granite grinding slab and wine vinegar was added dropwise until the consistency of double cream was reached. The paint was ground into a smooth paste, transferred to a glass jar and then washed eight times with distilled water to remove all traces of vinegar. No pigment discolouration as mentioned by Fortunato and others was noted, however vinegar grinding does result in compositional changes. These become evident when the differently treated pigment is analysed with XRD. Comparison of XRD results of the untreated lead white (black line), the lead white ground with water (blue line) and that ground with vinegar (red line), showed that water washing raised the proportion of cerussite by removing the other forms of lead salts, while washing with vinegar resulted in an even higher concentration of cerussite (Fig. 14.3). Although no strong difference in the resulting particle sizes or shapes can be noted between both washing methods when the pigment is made into oil paint and examined in cross section with SEM, grinding in vinegar does seem to result in a slightly raised proportion of small particles as compared to clumps of aggregated particles (Figs 14.4a, 14.4b).

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**Fig 14.4a** SEM-backscattered electron image of stack process lead white ground in water, paint prepared with poppy oil

**Fig 14.4b** SEM-backscattered electron image of stack process lead white ground in vinegar, paint prepared with poppy oil

SEM-BSE images: © Luc Megens, RCE

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22 Le Pileur d’Apligny 1779: 5–6, see Appendix 21, table 14.2.
14.5 Effect of washing on lead whites in mixture with calcium carbonate

Before the nineteenth century when barium sulphate became the main extender or adulterant for lead white, calcium carbonate was often mixed with lead white to produce cheaper grades of the pigment.\(^{23}\) Reconstructions show that when vinegar is brought into contact with lead white mixed with calcium carbonate, gas bubbles appear, as the calcium carbonate reacts with the acetic acid in the vinegar (Fig. 14.5). Barrow (1735) mentioned the appearance of bubbles during vinegar washing. Could this have been the effect that he observed?

Given this reaction, it was postulated that in some cases grinding with vinegar would have served to lower the calcium carbonate content in adulterated lead whites. To test this hypothesis, a mixture of lead white and calcium carbonate was ground into a fine, smooth slurry with either distilled water or with vinegar, then subsequently water washed to remove any trace of vinegar. Contrary to expectations, XRD did not indicate a significant shift in calcium carbonate content and the SEM backscatter images made from the paints prepared from the test materials do not reveal apparent changes in their visual characteristics (Figs. 14.6a, 14.6b). Neither does washing the lead white and calcium carbonate mixture in a large amount of vinegar result in significant changes to the calcium carbonate content.

14.6 Decanting

Pigment washing can be used for particle size selection through gravitational sedimentation: when suspended in a liquid, heavier particles settle more quickly.\(^{24}\) Empirical knowledge of this process is evident in several seventeenth-century recipes (Appendix 21, Tables 14.2 and 14.3). The methods described were simple: the pigment is suspended in water by stirring and the top part of the liquid is decanted or removed with a spoon before all particles have settled. Decanting was advised for lead white and earth pigments, amongst others.\(^{25}\)

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\(^{23}\) See Chapter 13.

\(^{24}\) The settling speed of particles depends not only on their mass and density, but also on their shape.

\(^{25}\) Kunckel 1707: 401-403 describes decanting a number of pigments. It is interesting to note that although he advises decanting lead white, zinnober, ‘Lasur’ [prob. Azurite] using clean source water, minium and ‘yellow lead’ are decanted using lye.
Figure 14.6a False colour SEM backscattered-electron image of paint made with lead white and chalk, water ground, paint prepared with poppy oil.

False colour image with all lead counts in red, and all calcium counts in green.

SEM-BSE False colour images © Luc Megens, RCE

Figure 14.6b False colour SEM backscattered-electron image of paint made with lead white and chalk, vinegar ground, paint prepared with poppy oil.

SEM-BSE False colour images © Luc Megens, RCE

Figure 14.7a SEM backscattered-electron image of a cross-section from paint made with the most coarse part of the lead white: the deposit after decanting.

Figure 14.7b SEM backscattered-electron image of a cross-section from paint made with decanted lead white (first decanting). Paint prepared with poppy oil.

SEM-BSE Images © Luc Megens, RCE
Decanting or sedimentation systems were developed further in an industrial setting during the nineteenth century (Appendix 21, Table 14.3). There, pigment was suspended in water and flowed through interconnected vessels of different heights. The heaviest particles settled first, and lighter particles travelled furthest.

Our experiments showed that sedimentation is very successful in separating smaller lead white particles from larger pigment particles or aggregates. A small amount of ground lead white was suspended in a large volume of distilled water. The liquid was stirred and the pigment was allowed to settle for 2 minutes. The top half of the liquid was then poured into a second beaker. There, the pigment was allowed to settle further. After 2 hours, half the water was transported into a third beaker, using a pipette in order not to disturb the lead white that had settled near the bottom. After drying, all of the lead pigments were ground with poppy oil and the resulting paints applied to Melinex.

A distinct difference in particle size is immediately evident in the SEM backscattered electron images (Figs. 14.7a, 14.7b). The decanted lead white bears a resemblance to the fine lead white used in the paint layers of Vermeer’s Art of Painting, which strongly suggests that such fine particles were selected through decanting. XRD shows that the fine lead white contains a higher proportion of cerussite than the deposit (Fig. 14.8). This demonstrates that decanting not only separates larger and smaller particles, but that the smaller particles are of a different composition than larger lead white particles or aggregates. This difference may in fact explain the tendency of traditionally prepared lead white to aggregate.

If the XRD results for the dry pigment samples can be used as an indication of the composition of the lead white in paint, they appear to contradict the results of Welcomme et al., who found a higher ratio of hydrocerussite to cerussite in the paint layers as compared to the ground layers of paintings (dated between 1512 and 1516) by Matthias Grünewald.

Investigation of the change of composition of lead white in paint is ongoing. Yet unpublished results from the HART project appear to show that the ratio of hydrocerussite to cerussite is lower in lead white paint tempered with linseed oil than in the dry pigment powder from which it was prepared. The different observations on the ratio of hydrocerussite to cerussite might also be linked to the equilibrium between the two in water, which can easily shift to either side under ambient conditions.

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26 Earlier experiments, repeated during the present research, ruled out the possibility that very fine grades of lead white could be produced by extensive grinding on the slab. Prolonged grinding did not succeed in breaking up the lead white agglomerates present in stack-process lead white (Carlyle 2006).

27 In a second series of particle size selection experiments, executed with the same batch of stack-process lead white, in the same laboratory and employing the same protocol for particle size selection, Marya Albrecht confirmed the shift towards a higher ratio of neutral cerussite to hydrocerussite. Albrecht 2012: 20.

28 Welcomme et al. 2007.

29 See Carlyle 2005 (unpublished): Chapter 2

30 Godelitsas et al. 2003.
Figure 14.8 Diffractogram demonstrating the shift in balance between cerussite and hydrocerussite caused by decanting.

Untreated lead white (blue), the deposit after decanting (green), the first decanted pigment (yellow), the pigment decanted last (red). Cerussite peaks are indicated with blue vertical lines, hydrocerussite peaks with red vertical lines. An increase in cerussite concentration is clear at the 25.4 position.

Diffractogram © Luc Megens, RCE

The use of decanted lead white with smaller particle sizes in preparatory layers seems unlikely. Our experiments show that the amount of lead white of a fine particle size is very small in comparison to the amount left as a deposit; using the decanted lead white for a layer that requires as much pigment as a preparatory layer seems an illogical purpose for this scarce and therefore precious material.

Use of the larger pigment particles deposited early in the decanting process for the preparation of preparatory layers however, does not seem far-fetched. Whether the use of the pigment deposit would have particular consequences for paint stability is however unlikely. XRD analysis does not show a significant difference between the cerussite content of the pigment deposit after decanting and the water-washed lead white that has not undergone decanting. The deposit, as all water-washed lead white, does have a lower hydrocerussite content than unwashed lead white, which also has a higher lead acetate content. Therefore the degree of washing is the most important factor influencing pigment composition, with unrefined (unwashed) pigment presenting a more chemically active state due to the presence of lead acetate and possibly, the higher hydrocerussite content.
14.7 Conclusions and future research

Reconstructions of water washing, vinegar grinding and decanting have provided more insight into the effects of these processing methods on visual characteristics of particles within paint cross-sections, as well as on their composition. The question whether oil paints containing only very fine lead white were created by extensive grinding or by decanting can now be decided in favour of decanting. The reconstructions have also shown all treatments to influence the balance between cerussite and hydrocerussite, all resulting in a higher proportion of cerussite. Vinegar grinding or washing does not remove calcium carbonate from adulterated lead whites.

The present research may only be considered as a first step, since it has not yet addressed the consequences of these processing methods for paint handling and for long-term paint stability.  

Are there any drawbacks to using less carefully washed or decanted lead white in preparatory layers? Does a relatively high proportion of hydrocerussite present a danger? During the nineteenth century, authors consider hydrocerussite more reactive than neutral lead carbonate. If this is indeed the case, preparatory layers may be more liable to be affected by saponification, since they are not likely to contain the more expensive, carefully washed and decanted qualities. Continued monitoring of the oil paints produced during the present research is required to compare the long-term stability of neutral cerussite and hydrocerussite within an oil binding medium. However in order to fully comprehend the effect of the use of lead white of different particle sizes, more factors must be taken into account. Besides considering the stability of the material itself, we must consider the whole structure of the painting. In the case of the Vienna Art of painting, Boon & Oberthaler (2010) concluded that the delamination which occurs is largely the effect of differences in flexibility between a rigid top layer that contains only small lead white particles and the lower layers, consisting of a much wider particle size range and thought to be more flexible as a consequence. The researchers determine that it is in fact the incompatibility in flexibility between both layers that creates internal tension, not the chemistry within the single paint layers themselves.

31 In her Master thesis at the University of Amsterdam, Albrecht has examined the handling properties of lead white consisting of only small particles. She concludes that lead white with very fine particles in oil produces very convincing scumbles over dark underlayers. Albrecht 2012 (unpublished), Albrecht and Stols 2013.

32 Mulder 1865: 302–3; Carlyle 2001: 260. Experiments undertaken by Rhodes and Van Wirt (1923) show that slightly basic lead carbonate retards the initial oxidation of linseed oil and does not promote final oxidation as much as a more basic lead white.

33 In the present set of reconstructions, linseed oil has been added to the lead white powder until a paint with a good consistency is made. As the amount of oil is required depends on particle size, different oil/pigment ratios were thus created. Naturally the amount of oil determines the amount of free fatty acids in the system. The availability of free fatty acids will influence the saponification rate. Therefore in future tests focusing on this particular aspect, the oil to pigment ratio must be measured and if possible kept constant throughout the series of experiments.

34 The severe delamination taking place is – for a large part –ascribed to incompatibility of the top layer, whose physical characteristics are compared to that of an enamel paint, with the more flexible lower layers created with pigments of a more diverse particle size. Boon and Oberthaler 2010: 236 Carlyle points out that 19th century sources report that lead hydroxide has a plasticizing effect on the paint. Its absence may in that case cause a cerussite-rich layer to be more brittle. Personal communication, Leslie Carlyle, September 2013.