'To prepare white excellent...': reconstructions investigating the influence of washing, grinding and decanting of stack-process lead white on pigment composition and particle size

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ABSTRACT

Historical recipes describe several refining methods to improve the quality of lead white, usually by grinding or washing with water and/or vinegar. Processing methods also include decanting (particle size separation based on gravitational sedimentation speed). This paper reports on reconstructions of such processing methods using historically accurate materials and techniques. Particle size separation through gravitational sedimentation is easy to accomplish. The size fraction thus produced bears a close resemblance to the very fine grade of lead white present in Vermeer’s *The Art of Painting* (Kunsthistorisches Museum, Vienna). Lead white is generally considered to be a basic lead carbonate, but it usually consists of basic and neutral lead carbonate, with small amounts of other lead salts. X-ray diffraction of the pigments produced with historically accurate techniques shows that all of the reconstructed processing methods influence the ratio of neutral to basic lead carbonate, favouring the formation of neutral lead carbonate.

Introduction

As the white pigment most commonly used for oil painting before the introduction of good quality zinc white or titanium white, lead white is discussed extensively in written sources. Prior to the 19th century, lead white was usually produced by the stack process: rolls or buckles of lead were exposed to dilute vinegar (acetic acid) inside glazed earthenware jars, which were buried in horse manure or spent tanning bark (both of which provided a source of heat and carbon dioxide through fermentation). The metallic lead was corroded by fumes from the dilute vinegar to form lead acetate, which in turn reacted with carbon dioxide to form (basic) lead carbonate. In large-scale production facilities, rows of earthenware jars, buried in the manure or tanning bark, were built up in stacks, which provides the derivation of the terms ‘stack process’ or ‘stack method’ and ultimately ‘stack lead white’. Although the 19th century saw the development of new production methods (such as the precipitated Clichy white and the German chamber process), artists continued to favour stack-process lead white for its excellent covering power and its rheology (Gettens et al. 1993).

Historical recipes not only described the pigment’s production, but dealt with its purification and adulteration, as well as its use in painting. An earlier publication on lead white production, quality and terminology, presents an overview of such recipes (Stols-Witlox 2011). To summarise briefly, historical sources ascribed quality differences to several parameters: not only was purity of the raw ingredients considered to be important, but also the reaction (corrosion) conditions as well as later processes such as washing, grinding and decanting of the pigment. While most painters were unable to influence reaction parameters personally as the pigment was generally produced by large-scale production, they could select lead white with particular characteristics and they were able to further process it themselves and thereby enhance 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 Tables 1–3). This information is highly relevant because paintings provide evidence of the use of different qualities of lead white and it is currently unclear whether this represents variables in manufacture, careful selection by the artist, or processing by the artist, their assistants or colourmen – or perhaps a combination of all these factors.

Lead white is usually referred to as basic lead carbonate, but Olby (1966) showed that it is in fact a mixture of cerussite (PbCO₃) and hydrocerussite (2PbCO₃·Pb(OH)₂); other lead salts such as plumboacrite (Pb₅O(OH)₂(CO₃)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 (Godelitsas et al. 2003), 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 and the quality of the starting materials (Homburg and Vlieger 1996: 39) – or on processing methods. Some reports in the late 19th and early 20th century state that the freshly produced pigment contained some residual lead acetate (Carlyle 2006: 15).

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 (BSE) images show particle morphology, they may be used to obtain an indication of whether or not lead white has been post-processed. This approach was employed successfully in a recent study by Boon and Oberthaler (2010) of The Art of Painting by Johannes Vermeer, dated to the 1660s. SEM BSE images demonstrate 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 has been employed with a considerably larger range of particle or aggregate sizes (see Fig. 1). Berrie and Matthew have reported similar differences in particle size (2011: 295).

How were different grades of lead white obtained, what was their exact composition and what are the possible consequences of their use for the visual characteristics of the final paint layer and for the way the paint ages? This paper 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.

Materials and methods

Reconstructions were based on a large collection of recipes for the production and processing of lead white from both published and unpublished sources, dating from c.1500 to 1900. This recipe collection was established by the Historically Accurate Reconstruction Techniques (HART) project. The recipe collection was expanded further by the first author in subsequent doctoral research. Recipes analysed for the present study include those that concern both lead white processing recipes describing professional manufacturing practice and recipes intended primarily for artists (Fig. 2). If available, first editions were consulted. Recipes copied or translated from earlier sources were included in the research, since they may provide information on the popularity of certain procedures.

The majority of recipes for processing lead white, especially those describing professional manufacturing methods, mentioned washing or grinding with water. The second largest group consists of instructions for grinding or washing with vinegar, the latter being mentioned mainly in recipes aimed at artists (Stols-Witlox 2011). Because of their relative frequency, these two methods were selected for comparative reconstructions.

Reconstructions were executed with traditionally prepared stack-process lead white, thoroughly washed with distilled water. Vinegar for grinding with the lead white was prepared from organic, sulphite-free red wine and vinegar culture (bacteria). Lead white pigments, further
processed by grinding with vinegar and/or further water washing, were subsequently made into oil paint by hand grinding with poppy oil extracted from a single seed lot from a single supplier. 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), and the oil paints were then analysed in cross-section with SEM-EDX. Colour measurements were made on the paint films using a Konica-Minolta spectrophotometer.
Historical recipes for washing stack-process lead white.

**Table 1** Historical recipes for washing stack-process lead white.

<table>
<thead>
<tr>
<th>Recipe</th>
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<tr>
<td><strong>To purify biaucca very fine with water.</strong> First grind the biaucca very soft with water; then wash 3 or 4 times and leave to dry on the stone, then gather and keep in paper. <em>Ad conciare la biaucca sottilissima con aqua.</em> Prima macinerai la biaucca sottilissima con acqua; poi la lava 3 o 4 volte e lascia secchere in su la pietra, et poi la tole et serba in una carta.</td>
</tr>
<tr>
<td><strong>Andriessen 1552. Viervoudig tractaetboeck.</strong> Kampen: Steven Joesens, 55</td>
</tr>
<tr>
<td>Lead white is ground on a hard stone with clean water and if you want it fair then when it is well ground leave it spread on that hard grinding stone and sprinkle on clean water and leave it to bleach in the hot sun and when it is dry humidiﬁy it again on the stone and grind it for a while and let it dry again and bleach [do] this up to four or ﬁve times. This is the most clean white that you can ﬁnd if you ﬁrst remove the blue lead that falls in during grinding that must always be removed or the lead white would truly stain. Looitwit wrytmen op ezen harden steen met schoon water ende wilmont schoont hebben so als welt gheserveis is laetemn uit ghespreyt liggen op die harde wrytsteen en besprengent met schoon water ende latent soo liggen ende bleken in die heete son ende alst drooge is salmone weder vochtych maencken op den steen ende wryvtem een poes ende laesten wederom drogen ende blyeken tot vier oft vijf reymen toe. Dat is tschoonste witt datmen kaw ghervijnden behouden dat ghi eerst wel uit glesen hebt blauwe loot datter in valt int wryten dat moettem alzijt wel waer nemen ende uit doen oft dat Looitwit souder werckelijck af smetten.</td>
</tr>
<tr>
<td>Then pound it, &amp; put it in a pignatto, &amp; for every libra of this flour [= lead white], add two ounces of water, &amp; put on the ﬁre while stirring it well together, leave on the ﬁre until smoke rises, then take it from the ﬁre, &amp; put it in the shape you like, &amp; put it in the sun, leave until it has dried well, then remove them from the mould, &amp; put it in a straw which will make ﬁne biaucca. dappo lo peestate, &amp; lo mettete in un pignatto, &amp; per ogni libra di questo ﬁore [= lead white], mettete oncia due d'acqua, &amp; penetelo al fuoco stemptionandolo bene insieme, lo farere star tanto al fuoco che levi il fuoco, poi cavatello dal fuoco, &amp; mettetella nella forma che voilet, &amp; penetelo poi al sole, lassandovelo ﬁn che sia beracciuto, Finalmente lo truote dalla forma, &amp; mettetella nella paglia che farà Biaucca ﬁna.</td>
</tr>
<tr>
<td>Biaccia cersese, white. When S. G. A. was to ﬁnish the quadro of Cleopat. A. M. ground Biaccia that is whyting whh water very well, then to take out the water ground it in Olio di lino washing it often, pouring on water constantly: This was to purify the Biaccia &amp; take out all the lead of whh tis made.</td>
</tr>
<tr>
<td><strong>Veen, J. van c. 1650. 'De wetenschap ende manieren om alderhande couleuren van say of sayetten te verwen.' The Hague: Royal Library, Ms. 133K44, 119</strong></td>
</tr>
<tr>
<td>Lead white is ground with clean water, if you want it beautiful so to bleach on the grinding stone, steeped and sprinkled with clean water in the hot sun and when it has dried it must again be humidiﬁed a little and ground and leave it to bleach and dry up to 5 times; Loodwit wryvtmen met schoon waeter, wilt gli't schoon hebben soo laedt het op een wryftsteen bleijcken, uijt gestroijt ende besprongt met schoon waeter inde heete sonneschijn ende aens, t drooge is salmen, t wederom een weijnig natten ende wrijven en laerter, t wederom blejcken en droogen tot , t op 5 mael toe;</td>
</tr>
<tr>
<td><strong>King, D. 1653–57. 'Secrets in the noble arte of miniatura or the art of limning.' London: British Library, Ms. Additional 12461, 38–9</strong></td>
</tr>
<tr>
<td>To prepare white excellent Take a good quantity of Seruse, and being grossly 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, taste the water and you shall ﬁnd it a salt harsh and unpleasant. Observe well the taste and poure the water of and cast it away. You shall ﬁnd this water to carry away with it a deal of grease rising on the top. Then add to as much more water, and then streire the ceruse as before and tasting it poure off the clear water retaining the bottom. This work you must reiterate some dozen times or more till by continuall washing you ﬁnd your water hath wash away all the salt out of the Ceruse and when you perceive that the water taste fresh as other water, then let it dry or setting the bason upon a soft ﬁre, let the residue of the water vaporise, and the ceruse being drie use of the fairest and reserve for yr use. Probatisimum</td>
</tr>
<tr>
<td><strong>Anon. 1668. The excellency of the pen and pencil. London: Dorman Newman, Richard Jones, 70</strong></td>
</tr>
<tr>
<td>Of those Colours that are to be Grown, and how to Grind them. In the last Section told you what Colours are to be Grown, which Washed, and which to be Steeped; it resteth now, to shew you how to grind those Colours that are to be grown; I shall not run over every Colour particularly, but shew you how to grind one Colour, which take as an example for all the rest. For our example in grinding of Colours, let us take the original of Colours, viz. Cersuse, or White-lead, there is little difference between them, only one is reﬁned, the other not. To grind it do thus; Take a quantitie thereof, or of any other Colour to be grownd, being cleansed from all manner of dirt or ﬁlth, which you must ﬁrst scrape off; then lay the Colour upon your Stone, and with your Muller bruise it a little, then put thereto fair spring-water, and between your Muller and Stone grind the Colour well together with the water till the Colour be very ﬁne, which when you ﬁnd to be enough, have in a readiness a great Chalk-stone, in which make certain troughs or furrows, into which pour your Colour thus grownd, and there let it rest till it be thorough drie, then take it out ans reserve it in papers, and those papers in boxes, for your use. contid.</td>
</tr>
</tbody>
</table>

_TO PREPARE WHITE EXCELLENT..._
Table 1
Historical recipes for washing stack-process lead white cont’d.

| Beurs, W. 1692. *De groote waereld in het klein geschildert.* Amsterdam: J. and G. Jansonius van Waesberg, 8 |

For this choose the thickest flakes, as the best, grind them in very clean and clear water on a good grinding stone, which must not be too hard or too smooth; and when it has been ground, put it on a piece of glass, on which the water must evaporate. When dry enough, grind with the best poppy oil, which surpasses nut oil, linseed oil and other known [oils], after which put it in a clean shell or bowl, and cover with clean water, to prevent drying; and so it can be kept; to be used, when needed [. . .]. The good non-ground lead white is prepared in the same way, as flake-white, but is easier to grind.

Daar toe dan kiezen uit de dikste Schulpen, als de beste, die men in zeer schoon en helder water vrijt op een goede keystone, die niet te hart of te glad wezen kan; en altsz is gewreven, zet meren op een stuk van een glas, daar op het water uit droogen moet. Als ze na droog genoeg is, vryvinnen die in de beste papaver oly, die de Noot-oly, Linzaat-oly en andre bekenden overtreff; waar na meren in een rein Schulpie of kommeijte doen, en er schoonwater op zet, om niet te verdrogen; en dus kynneze goed houden; om als t voogd is, gebruikte te [. . .]. T Goide ongelenen Lootwit bereiden op de zelte wyze, als het Schulp-wit; dog t is gemakelijker om vryven;

Smith, M. 1692. *The art of painting according to the theory and practice of the best Italian, French, and German masters.* London: Vendüe, 71

The instruments and Materials u’d in Painting and the preparing Colours to the pallat: Lead White

White Flakes being pick’d and scrap’d must first be ground very fine in water, afterwards Tempered on the stone with the muller with Nut-Oyle: then cover it with water in a gallipot or it will skin over. But so it must not be kept very long for the Oyle will grow Fat and make it unfit for use. For Deadcolouring you may grind white lead in Lynseed Oyle.


161: If you want to grind paints then first take some lead white to clean the stone and when it has been ground add some indigo, because this white is not pure enough to use, after this take lead white and it will be pure. The white you can grind with water, and let dry and temper with nut oil or linseed oil. Lead white is ground with urine or vinegar and when dry and you want to use it temper it with oil.

161: Alsom verwen vryvien wil zo neenst eerst wat loot-wit om den steen wat zayer te maken en als, t gewreven is zo doeter wat indigo bij, want dit wit dan niet zayer genoeg is om alleen te gebrauyen, daer na neemt ander loot-wit en die zal zayer zijn. T wit kon gij vryvien met water, en laeten droogen en temperent met met oly of lijn oly. Loot-wit vryft met pis of asijn en als gedroogt is en gij die wilt gebrauyen zo temperent met oly.

390:–94: Lead white is ground with clear water; and if you want to make it beautiful so it leave it spread on the stone after it has been ground and sprinkled with clean water and leave it thus to bleach in the hot sun and if it is dry it will again be humidified and re-ground for a while and then dried and bleached up to 4 to 5 times this is beautiful white and when you want to use it you will temper it with gum water. Note. If you grind this lead white you have to search and remove the lead which is normally in it or it would be contaminated from the start.

Looodwit wriffen met schoon water; wilmzten schoon hebben zo laet het wyt gepreget leggen op den steen als t gewreven is en besprengent met schoon water en latent zoostan bloeken in heete zon en als, t droosch is zal men t voedder vochtisch maken en vryvien wester een wyf tijts en wenckent en bloeken tot 4 of 5 maal toe dit is schoon wit en als men verwerken wil zy meest gehouden, en als die is gewreven zetten de zelte ook in de open lught, en als het is droog te verf men gom-water temperent. Nota. Alsom dit lootwit wriff z noot men het loot datter gemeeenlijk is in daar wyt zoeken of het zouden zonderlinge af besmet worden.


The lead white may also from the start be ground with water and some think this is better, but the Venetian white must from the start be ground in oil, because one cannot temper off the water from the white.

Het loods-wit magh oock wel van versten af aan met water gewreven worden dat vinden sommige beter, maar het venets wit moet van versten af in olie gewreven worden, om dat men het leeder daer niet uit temperen kan


Then one grinds these flakes on a hard stone, like porphory, with the muller & clear water, & as clean as possible to have a beautiful white; sometimes these flakes are covered with a grey or yellow material which must be grated off before grinding, which may be caused by the lead sheets that were not clean before they were enclosed in the pot. The lead white being well ground with water is left to dry, & you may keep it as long as you wish.

Eensyte en broeze ces ecailles sur une pierre dure, comme porphory, avec la molette & de l'eau claire, & le plus proprement qu'il est possible pour avoir de beau blanc; quelques fois ces ecailles sont couvertes d'une matiere grise ou jaune qu'il faut ratisser avant que de les broi, ce qui peut venir des lames de plomp qui n'étoient pas bien nettes par dessus quand on les a enfermées dans le pot. Le blanc de plomp étant bien broïé à l'eau enkelenberg, S. 1679–1738. *Aantekeningen.* Alkmaar: Municipal Archive, Mss. Eikelenberg

En ensuite on broi ces écailles sur une pierre dure, comme porphyre, avec la molette & de l'eau claire, & le plus proprement qu'il est possible pour avoir de beau blanc; ces écailles sont parfois couvertes d'une matière grise ou jaune qu'il faut ratisser avant de les broyer, ce qui peut venir des lames de plomp qui n'étaient pas bien nettes par dessus quand on les a enfermées dans le pot. Le blanc de plomp étant bien broyé à l'eau


138–9: Venetian lead or flake white must be ground with pure rain water, on a good stone, but especially with no other water, because no other water is good for the paints mentioned above.

Venedisch loof of schlip wit moet sterk met zuiver regenwater, op een goede steen gevreven worden, maar voor al met geen ander water, om dat geen ander water tot alle boven gemelde verwen goet is.
411–12: To make beautiful lead white.
Place it [i.e. the lead white] together in a mortar, and pour on a little water, and pound the paint for as much as half an hour, (it is better with water on a mill, such as potters use for their glazes) until it becomes as pulp, then put the paint with a spoon in one or two pots, and put it in the sun, and let it become hard, then it is ready.

Schoon Loot Wit te maken.

Doet die te zamen in een steene vysel, en get een wyng Water daarop, en stampet de verwe wel een half uur; (het is beter met water op een mole, als de potte bakkers tot haar verglaas gebruiken) tot het wert als pap, doet dan de verwe met een lepel in een of twee potten, en zet het in de zon, en laat het hart worden, dan is het gemaakt.

Lindenbergh, J.F. 1753. Nieuwe verlichter. Amsterdam: Steven van Esveldt, 2

Flake white. Preparation.

According to some there are two types, of which one is called Venetian, the other inland; but I have never seen more than one kind, which is one of the hardest materials used in paints, it is ground vigorously with pure rain water on a stone, a long time.

Schelpwit. Bereiding.

Hier van zyn volgens veele twee soorten, wier eene Venetsch, de andere Inlandsch genaamt word; dog ik hebbt nooit meer dan een soort gezien, 't selve is een der hardste stoffen die in de verven gebruikt worden, men wryft die sterk met schoon regenwater op een steen, een lange tyd.


There is no previous preparation necessary, in the case of white lead, to its use; except washing over where it is intended for more delicate purposes; but then indeed it is always best to substitute the flake white.

Buys, E. 1774. Nieu en Volkomen Woordenboek (10 vols), vol. 6: K-L. Amsterdam: S.J. Baalde, 754

This lead white is ground on a porphyr stone with a little water, and made into a dough, which is made in moulds into small pointed breads, which are dried for transport;

Men wryfd dit loodwit op den porphyr steen met een weinig water, en maakt er een deeg van, dat men in vormen tot kleine spitswyze brooden maakt, die men drogen laat om te ververen;


About the preparation, use and mixing of white paints.

Flake white. Preparation. It is ground vigorously with clean rain water on a stone, a long time.


men wryft het sterk met schoon regenwater op eenen steen, eenen langen tyd


White is made with lead white, or better, with flake white. It is first ground in water, then when it is very dry, with varnish, as thick, that it can be made into balls, make little bullets from it. It this way it is used in small quantities. For large quantities it is ground with linseed oil, cold water is poured onto the greasy mixture and ground so long until the water separates out. Because it becomes more clean and manageable with water, while considering the above, also a little of the greasiness is dissolved during grinding.


After the lead has been transformed into lead white through the vinegar vapors, it is ground on large grinding stones, which in large factories may be most economically driven by waterforce like machines, as tenderly as possible and humidified with water, so a thick pulp results. Then the lead white is cast in moulds, which are normally pyramid shaped, and dried in summer in the open air, in winter however in a moderately warm oven.


Nachdem das Blei durch die Dämpfe des Eßigs in Bleiweiß zernaget ist, so wird es auf groffen Reibestenen, die als Maschinen in einer großen Fabrik am vortheilhaftesten von Wasser getrieben werden können, auf das zarteste gerieben und dabei mit Wasser angefeuchtet, daß ein dicker Brei daraus wird. Sodann wird das Bleiweiß in Formen gebildet, die gemeiniglich pyramidenförmig sind, und im Sommer an der Luft, im Winter aber in einer mäßig warmen Stube getrocknet werden.

151: The factory grinds the lead white unmixed; however, it most commonly receives on the mill an addition of chalk. The pure flake white is poured onto the top millstone, humidified with water, and this is repeated more often, while it is ground. It flows through the channel at the top stone to the other stones, and is ground by all 4 stones. From the last grinding stone it is moved through a channel into a wooden vat, and from this scooped into triangular earthenware moulds which are approximately 4 to 5 zoll high, and has the same width on top. Here it stays as long, until it shrinks, and then it is placed on wooden boards and air-dried.

Die Fabrik reibt das Blaunweiß zwar auch unvermischt; allein, grösstenheils erhält es auf der Mühle einen Zusatz von Kreide. Das reine Schieferweiß schüttet man bloß auf den obersten Mühlestein, benetzt es mit Wasser, und wiederholt dieses zum äftens, während daß es gemalen wird. Es läuft durch gedachte Rinnen vom dem obersten Steine zu den drei übrigen, und wird von allen 4 Steinen vryft het sterk met schoon regenwater op eenen steen, eenen langen tyd

contd.
Oeconomische Courant, 15 October 1800. No. 167, 82

Economical knowledge. About LEAD WHITE, its fabrication, and trade.

The lead, chalked by the vinegar into lead white, is ground very fine on large grinding stones, which in a factory are most economically turned by water, crushed, and with water mixed into a thick pulp. Then the lead white is shaped in moulds, which ordinarily have the shape of a blunt sugar loaf; these loaves are dried in summer in the open air, and in winter in a moderately heated room.

Oeconomische kundigheden. Over het LOODWIT, het fabriceeren van, en den Handel met hetzelve.

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An unforfegetable white lead colour is made from lead white, which selected and all is ground on a porphyry, until it becomes blackish. Then take a pot filled with water, wash the lead white clean, and let it settle; and casting off the water, stir it again with vinegar; repeat this another one or two times, and you will have an excellently beautiful white, suited both for water- and oilpaints...

Een onvergelijkelijkt witte leegdeelt wordt gemaakt van leed-wit, dat uitgezocht en wel op een’ porfiersteen gewreven is, tot dat het zwartachtig wordt. Neem dan een pot vol water, wasch het leed-wit daar wel zuiver in af, en laat het bezinken; en het leed'er afgegoet en hebbende, roer het dan weder door met azijn; herhaal dit nog een of twee maal en, gij zult een uitstekend fraai wit, beide voor water- en olieverf geschikt, bekomen.


The *bianca* in the trade to purify, first pulvirese, and then pour on more than once boiling water; and it is very necessary to do this with Kremnitz [white], because it contains animal glue, from which it obtains its stiffness.

La bianca di commercio per depurarlo, si usas prima polverizzare, e poi sopra gettarvi più d’una volta dell’acqua bollente; ed è molto necessario fare questa operazione a quella di Kremnitz, perché contiene uno coll’ animale, donde ripete la sua tenacità.

Leuchs, J. 1825. *Vollständige Farben- und Farbekteunde.* Nuremberg: Handlung’s- Zeitung, 20–21

One clears away the manure, takes out the jars, scraps off the lead white adheeres to the metal *), after one has moistened it to prevent dusting, grinds it with some water to a thick pulp, which one leaves to stand for some days in a warm place, through which the remaining acids fully oxidise the metallic parts *), cleans it by washing or slaking **), if this is necessary, and has it ground *). Often it is finally slaked.

*) In Newcastle the lead passes with water through rollers, which remove the lead white. This prevents any dusting. The water is removed, after the lead white has settled, with pumps. The lead is reused or melted. If thin plates are used, they are normally completely corroded.

**) This however appears not to happen in all factories. Often also lead sugar crystals are found on the plates, like a white froth on the water, which contains much sugar of lead. In order not to lose this, one adds some potash, which decomposes it and creates a deposit of carboxylic lead (= lead white).

***) Slaking is operated as usual. One has a large, square tray, which has 7 to 9 compartements, which have the same size, but different heights (or the same amount of vessels of varying heights). The water stirred with lead white floats from one into another and it deposits in the later ones ever finer lead white. Good slaking substantially adds to the quality of lead white.

†) In Holland grinding is performed on three mills standing besides each other and operated with horses. The first grinds coarsely, the second finely, the third very finely. In Berlin the mills are placed on top of each other, so the ground [material] passes straight from one into the other. It would maybe be better to grind in tons, which spin around their axis, with the aid of iron balls.

The ground lead white is left under water for some time, then pressed into earthenware or sheet metal moulds, which have the shape of small conical hats, and left to dry first in these, then in the open air *) (during which very sulphurous vapours must be kept away) and then wrapped in paper.

*) In England also in rooms heated by vapour. One does not let them dry completely inside the moulds, because they would be difficult to remove.


†) In Holland geschichtet das malen auf drei nebeneinander stehenden und durch Eifere getriebenen Mühlen. Die erste malt grob, die zweite fin, die dritte ganz fein. In Berlin heben die Mühlen übereinander, so daß das Gemalene von einer gleich in die andere übergeht. Besser wäre es vielleicht in Tonnen, die um ihre Achse würden, mit Hulfe eiserner Kugeln, zu malen.


†) In Holland geschieht das malen auf drei nebeneinander stehenden und durch Pferde getriebenen Mühlen. Die erste malt grob, die zweite fin, die dritte ganz fein. In Berlin heben die Mühlen übereinander, so daß das Gemalene von einer gleich in die andere übergeht. Besser wäre es vielleicht in Tonnen, die um ihre Achse würden, mit Hulfe eiserner Kugeln, zu malen.


After approximately six weeks, one reveals the jars, and, unrolling the lead sheets, one finds them almost completely attacked and changed into a large amount of lead sub-carbonate and a little quantity of acetate of the same metal (salt which results from the combination of acetic acid with the lead). One separates these two salts from the lead portion which is still in its metallic state, one grinds and washes them; all that is acetate dissolves, while all that is sub-carbonate deposits as very dense layers of one or two centimetres thickness.

Au bout d’environ six semaines, on découvre les pots, et, en déroulant les lames, on les trouve presque entièrement attaquées et converties en une grande quantité de sous-carbonate de plomb et une petite quantité d’acétate de ce métal (sel provenant de la combination de l’acide acétique avec le plomb). On sépare ces deux sels des portions de plomb qui sont encore à l’état métallique, on les broye et on les lave; tout ce qui est acétate se dissout, tandis que tout ce qui est sous-carbonate se dépose sous forme de couches très-denses de un à deux centimètres d’épaisseur.

contid.
**Historical recipes for washing stack-process lead white cont'd.**

In about a fortnight the corrosion is finished, and the sheets of white lead are found near 1/4 inch thick, and covered in some places with crystals of sugar of lead. As much as can be got off by a moderate degree of force, is very carefully washed. This washing is esteemed the most delicate part of the whole manufacture; during the progress of it, a white scum appears which is taken off, and a little pearlash being added to it, it is changed into white lead, of a beautiful whiteness, and is sold for choice purposes: the remainder is mixed with a pure sulphate of barytes, brought from the Tyrol, in different proportions, according to the market for which it is designed.

Part of the sediment left in the cistern is well washed and produces a dull milk-white lead, with several portions of fresh water. Generally the washing is not continued to such exactness, because buyers prefer white lead that has a slight bluish tinge; now the copper contained in the litharge produces the colour, provided the settling is not washed too much. A grey tinge is sometimes preferred; which is produced by adding a small quantity of common ivory black, which must, however, be well mixed with the white lead.

**Silver white.** This white is used by easel painters, and is nothing but a lead white of the first quality, which one prepares with more care, and which one releases, by a large number of washings, of every possible impurity.

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**Grinding can, as said before, be executed in two manners, depending on whether hard or soft lead white shall be made. If hard [lead white] is made, the lead chalk dough or the dry lead white powder stirred with water is placed on the mill, while the stones are typically in motion, making 1½-1 turn per second. The pulp is scooped into the little "Sarge" [meaning unclear, probably hole in the centre of the stone] of the running stone and diameter 3½ Zoll, in which are placed on a drying rack and are shaken a number of times each day, to promote the loosening of the lead white bread from the mould. After 3 to 4 days the mould is turned and the bread is dried in summer in the warm air, in winter and in moist weather in a drying room heated with warm air. Finally the lead white is wrapped in blue paper.

Grinding to soft lead white can however also be executed in another manner, which facilitates rinsing and dividing. Because the lead chalk is ground with a lot of water, the ground material does not move like thick porridge, but as an easily movable liquid through the stones and leaks out by itself from the openings in the centers of the base stone. In this case the grinding stones can be easily set up in the following manner: they are placed around the vertical shaft like steps, so that whatever runs off the first stone, directly enters the second through a channel and then flows into the third and fourth and from there to the water removal vessel, in which the lead white, as explained before, is rinsed. This is the usual set-up of the German mills. During rinsing in large factories a substantial amount of lead is lost yearly, which is washed out and drains off with the washing water and lead acetate, and is too dilute to be further usable. This loss can amount to some percents. To prevent this, one can do two things. One adds to the first water, with which a lead white is stirred, one “Maß” of a crystal soda solution, which results in a precipitation, in which the dissolved lead settles as carboxylic lead oxide. Or – which is the best method – one directs all the draining wash water into a slake, to which an excess of chalk or carboxylic chalk has been added, where the lead then settles bit by bit as lead white and calcium carbonate dissolves in return. After a long time one examines the contents of the slake and decides whether it is possible to separate it, and ultimately some lead white has accumulated inside, and then rinses it again.

Das Vermahlen kann man, wie schon gesagt, auf zweierlei Weise vor sich gehen, je nachdem hartes oder weiches Bleiweiß dargestellt werden soll. Wird hartes dargestellt, so kommt der Teig des Bleikalks oder das mit Wasser angerührte trockene Pulver des Bleiweisés auf die Mühle, während sich die Steine gewöhnlich so bewegen, daß sie in der Secunde 1½ - 1 Umdrehung machen. Man schießt den Brei mit Hilfe eines langgestielten kupfernen Löffels in die kleine Sarge des Läufers und gibt so viel auf, bis die Sarge voll ist. Es dauert dann einige Zeit, bis deren Inhalt niedergesunken ist, worauf man wieder nachfüllt, bis nach und nach eine Partie, z. B. 10 Centner durchgegangen sind. Ein arbeiter kann bis 5 Steine, die neben einander stehen, bedienen. Was in der der Sarge des Bodensteines sich von Gemahlensamen ansammelt, wird durch ein Schaufelchen ofters nach vorn in den Ablauf geschafft, wo es in einen kleineren Ständer fließt. Bei dem ersten Mahlen ist es häufig nötig, den Stein etwas höher zu stellen, denn weil die Masse sehr dick wird, läuft sie nicht ganz unter und durch die beiden Steine. Wenn Alles durchgemahlen ist und man das Gemahlene einen zähen Brei darstellt, so wird der Stein durch Nachspülen von Wasser rein gemahlen, die Bodensteinarme auch ausgewaschen, womit sich eines groben Haarpinsels oder einer Bürste bedient, und nun wird derselbe Brei noch einige Male auf eben dieselbe Weise bei enger gestellten Steinen hindurch- und fein gemahlen. Besser ist es jedoch, und so wird es auch meistens gehalten, daß man den rohen Bleikalk stets einen Stein passieren läßt und das Feinmahl en an einigen anderen Gängen, die zu gleicher Zeit in Bewegung sind, ausgeführt wird, dann wird dasjenige, was vom ersten Steine kommt, auf den zweiten, von da auf den dritten und vierten Stein geschöpft und das Mahlen geht dann regelmässig und ununterbrochen fort.

Soll weiches Bleiweiß dargestellt werden, so kann man zwar sowohl bei reinem Bleiweiß, als den gemischten Sorten bis zum Fertigmahl en eben so verfahren, aber damit es sich hart werde, ist ein sorgfältiges Auswaschen unumgänglich erforderlich. Zum Auswaschen hat man dann eine Annahme grosser Steine nötig, die um so besser, je grösser sie sind. Diese Steine füllt man mit Wasser, bringt das gemahlene Bleiweiß hinein und rührt es wohl auf, was aber schwer ist, weil es sich nicht gut zerteilt. Dann läßt man es absitzen, bis die Flüssigkeit klar ist, welche man darauf ablaufen läßt. Dieses Aufspüren mit frischem Wasser, Absetzenlassen und Abziehen wiederholt man einige Male. Als dann bringt man den sich sehr dick ansetzenden Bleiweißbrei in Filter, von da auf Pressen, um das Wasser zu entfernen und dann in ungezählten Stücke zum Trocknen an der Luft oder in Trockenstuben, je nachdem dazu die Einrichtungen vorhanden sind.

Das Vermahlen zu weichem Bleiweiß kann aber auch von vorn herein auf eine Weise erfolgen, wodurch das Auswaschen und Zerteilen leichter vor sich geht. Der Bleikalk wird nämlich mit viel Wasser vermahlen, so dass das Gemahlene nicht als dicker Brei, sondern als eine leicht bewegliche Flüssigkeit durch die Steine und von selbst aus den Ausschüttungen der Sarge die Bodensteinarme herausläuft. In diesem Falle ist leicht eine solche Anordnung der Mahlgänge möglich, daß sie um das vertikal stehende Tribier herum stehen- oder treppenweise aufgestellt sind, so dass dasjenige, was vom ersten Steine abläuft, direct durch eine Rinne zu dem andern Stein tritt und so zum dritten und vierten und von da in die Abwässerungsstanden, worin das Bleiweiß, wie vorhin schon erwähnt, abgewaschen und gewaschen wird. Dies ist die gewöhnliche Anstellung der deutschen Mühlen.

Water washing

A particularly detailed description of how to wash lead white is provided in a recipe entitled ‘To prepare white excellent’ recorded by Daniel King (1653–57: 38–9):

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, taste 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 continual washing you find your water hath washt away all the salt out of the Ceruse.

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. An overview of water-washing recipes within the period under investigation (Table 1) shows that the main methods used were either washing with large amounts of clean water, repeated grinding with water on the slab, or a combination of both treatments. Comparison of XRD analyses of unwashed and water-washed lead white confirmed the findings of the
Table 2 Historical recipes for processing lead white with vinegar.

<table>
<thead>
<tr>
<th>Source</th>
<th>Recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fortunato of Rovigo, 1607 [1659–1711]</td>
<td>To render bianca extraordinarily more white. Take lead white in flakes, choose the most beautiful, and grind well on the marble with vinegar, and it will become black; then take an earthenware beaker full of water, and wash your white well, then let it settle well at the bottom, and pour off the water by inclination. Return to grinding with vinegar and wash; and having done this approximately 3 or 4 times, you will have a bianca that will be perfectly beautiful for miniature painting, as well as oil painting.</td>
</tr>
<tr>
<td>Buc'hoz, M. 1786.</td>
<td>If you want to grind paints then first take some lead white to clean the stone and when it has been ground add some indigo, because this white is not pure enough to use, after this take lead white and it will be pure. The white you can grind with water, and let dry and temper with nut oil or linseed oil. Lead white is ground with urine or vinegar and when dry and you want to use it temper it with oil.</td>
</tr>
<tr>
<td>Le Pileur d'Apligny 1779.</td>
<td>To render lead white extraordinarily fine. Take lead white in flakes, choose the most beautiful, &amp; grind these flakes well on the stone, with vinegar, &amp; it will become black; then take an earthenware beaker full of water, &amp; wash your white well, then let settle well, &amp; pour off the water by inclination; grind again with vinegar &amp; wash again, doing this three or four times, &amp; you will have a white that will be perfectly beautiful both for miniature painting and for oil painting.</td>
</tr>
<tr>
<td>Barrow, J. 1735.</td>
<td>But if you use white lead, first rectify it with white wine vinegar, this will cause a fermentation, and the white will soon settle; then pour off the water, and wash it with common water. The method of washing it is thus: Put the powder into a glass of water, stir it about, and presently pour off the water, while it is white, into some other clean glass vessel or letsettle, &amp; then pour off the water from it, and it will be excellently fine. Some say it is better, if some rectified spirits of wine be pour’d on it, which will clear it from any dross that may be in it; this (as it is very probable) must be pour’d off, when the spirit of wine has done its work.</td>
</tr>
<tr>
<td>Le Pileur d'Apligny 1779.</td>
<td>When you wish to use ceruse in painting, you have to purify it with white vinegar: so it is ground on a porphyry, while wetting it with vinegar, until it is an impalpable powder: then one places it for washing in a vase filled with water, which one shakes for some time: one lets settle the largest particles, then one transfers the white water to another vessel: one lets precipitate the white, &amp; then one decants the water that floats on top. One obtains by this method a very beautiful and very fine white, cleansed of anything that might change its whiteness: the reason is that this white is not subject to darkening because of the badly dissolved lead particles that it contains, or at least very disposed to altering itself by the least contact with the air; the vinegar achieves the complete dissolution of these particles, much better than a mineral acid, because it does not contain phlogistique, at least also developed: it is good for this reason only to purify the amount that you need.</td>
</tr>
<tr>
<td>Fortunato of Rovigo 1967 [1659–1711]</td>
<td>Or choose the most beautiful lead white in flakes, very white &amp; very soft: grind it on a stone with vinegar, it will become black; but when you have washed it in very clear water, let it settle well; pour off the water by inclination, then grind again with vinegar, &amp; wash again; repeat the same four to five times; it will become very beautiful &amp; very bright: it is very good for illumination &amp; for painting in oil.</td>
</tr>
</tbody>
</table>

*TO PREPARE WHITE EXCELLENT...*
152: When one uses lead white for painting, it must be cleaned with white wine vinegar. For this purpose one grinds it on a porphyry, after having moistened it with this wine vinegar, until it has become an impalpable powder. Then it is poured into a vessel filled with water for washing, which is shaken for a while, then the coarsest particles are left to settle at the bottom; after that the still whitish water is poured into another vessel, and the white, which is still in the water, is left to settle at the bottom, after which one decants the supernatant water. In this manner one obtains a very beautiful and fine white, which above all has been cleaned of anything, which may harm its whiteness and may change it. Because this white only tends towards grey or black, because the lead particles which remain inside either have not been dissolved completely, or have the tendency to change back into lead upon the least contact with air. The wine vinegar however helps to dissolve these lead particles completely, and even better than any mineral acid would, because this does not have an inflammable nature, at least not openly.

Venn man das Bleiweiff zum Malen gebrauchen will, so muß es mit weiflgen Weinflß gereinigt werden. Man reibt es demnach auf einem Porphyriefstein, nachdem man es mit diesem Weinflß angefeuchtet hat, so lange, bis es zu einem unfehlbaren Pulver geworden ist. Hierauf wird es zum Abwaschen in ein Gefäß voll Wasser geschüttet, welches man eine Zeitlang schüttelt, läßt es eine kurze Zeit die grifflsten Theilchen zu Boden fallen, und gießet das noch weiflgelahrte Wasser in ein anderes Gefäß, und läßt alles Weißt, das noch in dem Wasser ist, zu Boden setzen, worauf man das darüberrastende Wasser abgibt. Auf diese Art erhält man ein sehr schönes und feines Weißt, welches von allem entlediget worden, was seiner Weißf Schaden zu und solche verändern könnte. Denn dieses Weißt fällt nur deswegen gern in das graulichte oder schwärzliche, weil die Bleitheilchen, die darinnen sind, entweder nicht genügsam aufgelöst worden, oder doch zum wenigsten bei der geringsten Berührung der Luft sehr gejagt sind, sich wieder in Blei zu verwandeln. Der Weinflß aber hält dazu, daß diese Bleitheilchen völlig aufgelöst werden, und zwar weit besser, als es eine mineralische Säure thun würde, weil derselbe kein brennliches Wesen, wenigstens nicht offenbar mit sich führt.

153: see Table 1.

Table 2. Historical recipes for processing lead white with vinegar. cont’d.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anon. 1794.</td>
<td>Färbkabinett. Vienna/Prague: Verlage der von Schönfeldschen Handlung</td>
</tr>
</tbody>
</table>

HART project: lead acetate was indeed removed from lead white by repeated washing (Carlyle 2006: 25–6). Furthermore, our reconstructions showed a shift in the balance between cerussite and hydrocerussite, with the washed lead white containing less hydrocerussite.

Vinegar grinding

As noted above, besides water washing, artists were often 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 discoulour 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) noted that rectified vinegar caused ‘fermentation’ of the lead white (presumably the formation of gas bubbles). Table 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 time period under investigation.

A series of grinding experiments following the instructions of Le Pileur d’Apligny was executed with unprocessed
Table 3  Historical descriptions for pigment decanting or other methods of particle size election.

<table>
<thead>
<tr>
<th>Year</th>
<th>Author</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1620</td>
<td>Mayerre</td>
<td>White ground washed, then washed &amp; allowed to settle, decanting the turbid water, makes a deposit that is very beautiful, &amp; dies less than the deposit.</td>
</tr>
<tr>
<td>1623</td>
<td>King</td>
<td>Secret in the noble arte of miniature or the art of limning.</td>
</tr>
<tr>
<td>1668</td>
<td>Anon</td>
<td>The excellency of the pen and pencil.</td>
</tr>
<tr>
<td>1770</td>
<td>Anon</td>
<td>Nauwkeurige beschryving van het schilderen der zwarte konstprints.</td>
</tr>
<tr>
<td>1794</td>
<td>Anon</td>
<td>Wiener Farbenkabinet.</td>
</tr>
</tbody>
</table>

To prepare white excellent...

...cont'd.

*TO PREPARE WHITE EXCELLENT...*
Table 3 Historical descriptions for pigment decanting or other methods of particle size evaluation (cont’d).

<table>
<thead>
<tr>
<th>Source</th>
<th>Method or Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mérimeé, M.F.L. 1830. De la peinture à l’huile. Paris: Mme. Huzard, 228–9</td>
<td>Stack-process lead white and vinegar (Le Pileur d’Apligny 1779: 5–6, table 2). Dry,</td>
</tr>
<tr>
<td></td>
<td>unwashed pigment was transferred to the granite grinding slab and wine vinegar was</td>
</tr>
<tr>
<td></td>
<td>added dropwise until the consistency of double cream was reached. The paint was</td>
</tr>
<tr>
<td></td>
<td>ground into a smooth paste, transferred to a glass jar and then washed eight times</td>
</tr>
<tr>
<td></td>
<td>with distilled water to remove all traces of vinegar. No pigment discoloration as</td>
</tr>
<tr>
<td></td>
<td>mentioned by Fortunato was noted, however vinegar grinding did result in</td>
</tr>
<tr>
<td></td>
<td>compositional changes. These became evident when the difference in the resulting</td>
</tr>
<tr>
<td></td>
<td>particle sizes or shapes could be compared to clumps of aggregated particles (Fig.</td>
</tr>
<tr>
<td></td>
<td>4a and b).</td>
</tr>
</tbody>
</table>

Effect of washing on lead whites in mixture with calcium carbonate

Before the 19th 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 (Stols-Witlox 2011). Reconstructions show that when pigment 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. 5).

Given this reaction, it was postulated that in some cases the lead in pigments containing lead white to result in an even higher concentration of cerussite (Fig. 3). Although no strong difference in the resulting particle sizes or shapes could be noted between both washing methods, grinding in vinegar did seem to result in a slightly raised proportion of small particles as compared to clumps of aggregated particles (Fig. 4a and b).
the SEM BSE images made from the paints prepared from the test materials do not reveal apparent changes in their visual characteristics (Fig. 6a and b).

**Decanting**

Pigment washing can be used for particle size selection through gravitational sedimentation: when suspended in a liquid, heavier particles settle more quickly. Empirical knowledge of this process was evident in several 17th-century recipes (Tables 2 and 3). The methods described were simple: the pigment was suspended in water by stirring and the top part of the liquid was decanted before all particles had settled. Decanting was advised for lead white and earth pigments, among others. Decanting or sedimentation systems were developed further in an industrial setting during the 19th century (Table 3). There, pigment was suspended in water and flowed through interconnected vessels of different heights. The heaviest particles settled first and the lighter particles travelled farthest.

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 two minutes. The top half of the liquid was then poured into a second beaker. There, the pigment was allowed to settle further. After two 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 lead whites were ground with poppy oil and applied to Melinex.

A distinct difference in so-called particle size is immediately evident in the SEM BSE images (Fig. 7a and b). The decanted lead white bears a resemblance to the fine lead white used in the paint layers of Vermeer’s *The Art of Painting*, which strongly suggests that such fine particles were selected through decanting. XRD showed that the fine lead white contains a higher proportion of cerussite than the deposit (Fig. 8). This demonstrates that decanting not only separates larger and smaller particles, but that the smaller particles are of a different composition from 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. (2007), 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 (Godelitsas et al. 2003).

**Conclusion and future research**

Our 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 of 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. Our reconstructions have shown all treatments to influence the balance between cerussite and hydrocerussite, all resulting in a higher proportion of cerussite.

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 benefits to using lead white with a high proportion of cerussite? Colour measurements indicate that after two months of natural ageing, vinegar-treated lead whites have yellowed considerably more than water-washed
lead whites. A higher proportion of cerussite therefore does not necessarily create a whiter paint. Research by de Behault (2010) showed that small-sized lead white particles may have been selected by artists wishing to optimise blue-hued scattering effects, as seen for instance in the cool grey skin on blue grapes.

Yet another reason to post-process lead white may have been to enhance pigment stability. During the 19th century, authors considered hydrocerussite more reactive than neutral lead carbonate. 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. Different ageing characteristics are to be expected: the white top layer in the marble floor tiles of Vermeer’s *The Art of Painting*, created with very fine lead white, demonstrated severe delamination, which – for a large part – was ascribed to incompatibility of this layer with the more flexible lower layers created with pigments of a more diverse particle size (Boon and Oberthaler 2010: 236).

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Notes

1. Plumbonacrite is reported to transform easily to hydrocerussite and is not always detected in lead white samples (Olby 1966). Its presence was analysed with XRD by Hallebeek of the (then) Netherlands Institute for Cultural Heritage in lead white samples analysed for the HART project (Carlyle 2006: 50).

2. 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.


4. Produced by Jef Seynaeve, Belgium, for the HART project.

5. Distilled water was added to previously crushed lead white. Pigment and water were stirred for two 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: 25–6).

6. 50 ml of vinegar culture (Brouwland of Everlo, Belgium, purchased 18/9/2010) was added to 500 ml sulphite-free organic red wine (Stellar Organics, Shiraz, South Africa, imported from Coenecoop Wine Traders B.V., 2742 RC Waddinxveen). The liquid was allowed to acidify during four 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).

7. Poppoy oil produced by the HART project; see Carlyle (2006) for details.

8. The crystalline phases were analysed by 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.

9. JEOL 5910LV with thermo scientific energy-dispersive X-ray spectrometry system with Noran System Six software.

10. Konica Minolta CM-2600d spectrophotometer, white calibration 7004450.


12. The settling speed of particles depends not only on their mass and density, but also on their shape.

13. 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 (Carlyle 2006).

14. Procedure according to ASTM 2001 standard to determine the Yellowness Index (YI) E313-73: illuminant D65 (daylight, colour temperature 65°), 10° observer (CIE 1964), three automatically averaged measurements in three different locations. Vinegar-treated lead whites had a ΔYI roughly twice as large as the water-treated lead whites.

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

References


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