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

Maartje Stols-Witlox, Luc Megens and Leslie Carlyle

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 (\(\text{PbCO}_3\)) and hydrocerussite (\(2\text{PbCO}_3\cdot\text{Pb(OH)}_2\)); other lead salts such as plumbonacrite (\(\text{Pb}_5\text{O}((\text{OH}),\text{CO}_3)\)) 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.
Table 1  Historical recipes for washing stack-process lead white.

<table>
<thead>
<tr>
<th>Recipe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pomaro, G. 1500–1600. I ricettari del fondo palatino della bibliotecca nazionale centrale di Firenze. Milan: Giunta Regionale Toscana Editrice Bibliografica, 98 (Pal. 796: c. 5v)</td>
</tr>
<tr>
<td>To purify biacca very fine with water. First grind the biacca very soft with water; then wash 3 or 4 times and leave to dry on the stone, then gather and keep in paper.</td>
</tr>
<tr>
<td>Ad conciare la biacca sottilissima con aqua. Prim a macinerai la biacca sottilissima con acqua; poi la lava 3 o 4 volte et lassala secchere in su la pietra, et poi la tolle et serba in una carta.</td>
</tr>
<tr>
<td>Andriessen 1552. Viervoudig tractaetboek. Kampen: Steven Joessen, 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 humidify 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.</td>
</tr>
<tr>
<td>Lootwit wrytmen op een harden steen met schoon water ende wilment schoon hebben so alst wel ghewreven is laaten uim ghewrept liggen op die harde wrifsteyne en besprengent met schoon water ende latent soo liggen ende bleken in die heete son ende alst drooge is salment weder vochtich maecchen op den steen ende wrjwint een poes ende laetsten wederom drogen ende bleken tot vier oft vijf reysen toe. Dat is tschoonstest wit datmen kav ghewijndern behouden dat ghie eerst wel uit gelesen hebblauwe lost datter in vab int wrijven dat mostuiten alzijt wel waer nemen ende uit doen oft dat Lootwit souder werkelyck 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 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 it from the mould, &amp; put it in a straw which will make fine biacca.</td>
</tr>
<tr>
<td>Le white is ground with clean water, if you want it beautiful so leave it to bleach on the grinding stone, strewed 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;</td>
</tr>
<tr>
<td>Biacca ceruse, white. When S. G. A. was to finish the quadro of Cleopat. A. M. ground Biacca that is whyting wht 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 Biacca &amp; take out all the lead of wht tis made.</td>
</tr>
<tr>
<td>Veen, J. van c. 1650. 'De wetenschap ende manieren om alderhande coulereun van say van sayetten te verweren.' The Hague: Royal Library, Ms. 133K44, 119</td>
</tr>
<tr>
<td>Lead white is ground with clean water, if you want it beautiful so leave it to bleach on the grinding stone, strewed 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;</td>
</tr>
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<td>Bicca ceruse, white. When S. G. A. was to finish the quadro of Cleopat. A. M. ground Biacca that is whyting wht 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 Biacca &amp; take out all the lead of wht tis made.</td>
</tr>
<tr>
<td>Le white is ground with clean water, if you want it beautiful so leave it to bleach on the grinding stone, strewed 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;</td>
</tr>
<tr>
<td>King, D. 1653–57. 'Secrets in the noble arte of miniatura or the art of limning.' London: British Library, Ms. Additional 12461, 38–9</td>
</tr>
<tr>
<td>To prepare white excellent. Take a good quantity of Senure, 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 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 taste and pour 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 pour off the clear water reserving the bottom. This work you must iterate 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 vapourise, and the ceruse being drie use of the fairest and reserve for yr use. Probatissimum</td>
</tr>
<tr>
<td>Anon. 1668. The excellency of the pen and pencil. London: Dorman Newman, Richard Jones, 70</td>
</tr>
<tr>
<td>Of those Colours that are to be Ground, and how to Grind them. I have in the last Section told you what Colours are to be Ground, which Washed, and which to be Steeped: it resteth now, to shew you how to Grind those Colours that are to be ground; 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.</td>
</tr>
</tbody>
</table>
| For our example in grinding of Colours, let us take the original of Colours, viz. Ceruse, 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.
**Table 1** Historical recipes for washing stack-process lead white

<table>
<thead>
<tr>
<th>Source</th>
<th>Recipe Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beurs, W. 1692. <em>De groote waereld in het klein geschildert.</em> Amsterdam: J. and G. Jansonius van Waesberg, 8</td>
<td>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.</td>
</tr>
<tr>
<td>Maar 138–9: <em>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.</em> Leiden: Wed. en Zoon van Jan vander Deyster, 1747.</td>
<td>Daar toe dan kiesten u uit de dikste Schulpen, als de beste, die men in zeer schoon en helder water vrijft op een goede keystone, die niet te harte of te glad wezen kan; en alsze is gewreven, zet menze op een stuk van een glas, daar op het water uit droogen moet. Als ze na droog genog is, vryst men dens die in de beste papaver oly, die de Noö-oły, Lijnsaat-oły en alde bekenden overtreft; waar na menze in een rein Schulpie of kommezie doen, en er schoonwater op zet, om niet te verdrengen; en dus komen ze zeer goed houden; om alsz, t voedig is, gebruikt te […]</td>
</tr>
</tbody>
</table>
17/01/2012 10:18

411–12: To make beautiful lead white.
Place it (= 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 zazen in een steene vysel, en get een wyng Water daarop, en stampt de verwe wel een half uur, (het is beter met water op een mole, als de potte bakkers tot haar verglaas gebraukken) 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 verlijker. 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 hebbe nooit meer dan een soort gezien, ‘t selve is een der hardste stoffen die in de verwen gebruuk 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. Nieuw en Volkomen Woordenboek (10 vols), vol. 6: K-L. Amsterdam: S.J. Baalde, 754
This lead white is ground on a porphyry stone with a little water, and made into a dough, which is made in moulds to small pointed breads, which are dried for transport;

Men wryft dit loodwit op den porphyr steen met een weinig water, en maakt, er een deeg van, dat men in vormen tot kleine spitsvrye broODen maakt, die men drogen laat om te vervooren;

About the preparation, use and mixing of white paints.

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

White is made with lead white, or better, with flake white. It is first ground in water, when then it is very dry, with varnish, as thick, that it can be made into balls, make little bullets from it. This way it is used in small quantities. For large quantities it is ground with linseed oil, cold water


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.

Siebenter Abschnitt. Von der weifen Farbe. 1 Weisses Bleiweiß.
Nachdem das Blei durch die Dämpfe des Efgis in Bleiweiß zernaget ist, so wird es auf großen Reibesteinen, die als Maschinen in einer großen Fabrik am vorteilhaftesten von Wasser getrieben werden können, auf das zarteste gerieben und dabei mit Wasser angefeuchtet, daß ein dicker Brei daraus daraus. Sodann wird das Bleiweiß in Formen gebracht, 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, 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 of 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.


cont'd.
Die Zubereitung mit Wasser macht das Schieferweiß reiner und weißer, als wenn man es sogleich mit Oel abreibet. Dieses schöne Weiß wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.

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

<table>
<thead>
<tr>
<th>Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maar</td>
<td>Das man wieder zum frischen Ansatz brauchen kann.</td>
</tr>
<tr>
<td>Lóodwit</td>
<td>Das Bleiweiß zum Versenden fertig. Je mehr die Masse mit Wasser gewaschen wird, desto weisser wird das Bleiweiß, und bei dem Zusatz von Kreide.</td>
</tr>
<tr>
<td>Loodwit</td>
<td>Am gewöhnlichsten so: mann nimmt Bretter mit Löcher, in die man kegelförmige irdene Gefäße steckt. Das Loch, das dies Gefäß unten haben muß, der nicht ausgeholte Stein ein Loch haben, um einen Trichter hineinstecken zu können, durch welchen die Masse hineingegossen wird. Man hat nun noch einene Stein, von der Form einer Halbkugel, der grade in die Höhlung des andern hineinpaßt. In der Mitte hohl aushauen, oben am Rande wird eine kleine Rinne eingehauen, durch welche die Masse während des Reibens in ein anderes untergestelltes Gefäß fließt. Diese Mühle kann man auch im Kleinen machen, und zwar so: Man läßt einen großen Stein, wie eine halbe Kugel, hoch aushauen, oben am Rande eine kleine Rinne eingehauen, durch welche die Masse während des Reibens in ein anderes untergestelltes Gefäß fließt. Dieses schöne Weiß wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.</td>
</tr>
</tbody>
</table>

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

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

The lead, chalcked by the vinegar into lead white, is ground very fine on large grinding stones, which in a factory are most economically turned by water, or 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 kundigeden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelve.

**Leeu, c.1800. Over teken- en schilderkunst & naad aan kunstverzamelaars. [Delfshaven?], 4**

To render white, whatever sort, unequally beautiful it is ground clean in water, dried and then crushed and ground with fresh poppy oil.

**Brodhagen, P. 1802. Anleitung zur Technologie (3 vols).**

Oeconomische kundigeden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelve. By water, or 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 kundigeden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelve.

**15 October**

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**17 October**

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**18 October**

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**19 October**

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, or 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 kundigeden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelve. By water, or 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 kundigeden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelve.
An unforgettable 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...

A very unguerlissige white leadcoke is gemaakt van lood-wit, dat uitgezocht en wel op een' porfiersteen gewreven is, tot dat het zwartachtig wordt. Neem dan een pot vol water, wasch het lood-wit daar wel zuiver in af, en laat het bezinken; en het water er afgegeven hebende, roer het dan weder door met azijn; herhaal dit nog een of twee maleen, en zij gult een uiteenlopende fraai wit, beide voor water- en olieverwen geschikt, bekom.

The biaçca in the trade to purify, first pulvérise, 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.

Man räumt dann den Mist weg, nimmt die Topf heraus, schaut das an dem Metall hängende Bleiweiß ab †), nachdem man es befeuchtet hat, um das Stauben zu verhüten, stößt es mit etwas Wasser zu einem dicken Brei, den man einige Tage an einem warmen Orte rotzig stehen läßt, damit die anhängende Säure die metallischen Theile noch vollends oxidirt **), reinigt es dann durch Abwaschen oder Schlämmen ***) wenn dies nöthig ist, und läßt es malen †). Oft wird es zuletzt noch geschlärmt.

De kunst van tekenen en schilderen in waterverwen, enz. Leiden: A. and J. Honkoop, 83


TO PREPARE WHITE EXCELLENT...

***) Slaking is operated as usual. One has a large, square tray, which has 7 to 9 compartments, 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 Holland 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 washed or melted. If thin plates are used, they are normally completely corroded.

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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 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 washed or melted. If thin plates are used, they are normally completely corroded.


After approximately six weeks, one reveals the jars, and, unrolling the lead sheets, one finds them almost completely attacked and changed into a large quantity 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, 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.

Ash bunt en vieren six semaines, on découvre les pots, et, en déroulant les lames, on les trouve presque entirely attaquées and convertites en une grande quantité de sous-carbonate de plomb et une petite quantité d'acétate de ce métal (sel provenant de la combinaison 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.

contd.
Table 1 Historical recipes for washing stack-process lead white cont’d.

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<td>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.</td>
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<td>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.</td>
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| Maar Zoll horizontal granite stones, the pulp put into the upper wide end of conical, non glazed jars of height 5 in, and diameter 3½ 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. |

| Vergnaud, A.D. 1831. Manuel du peintre en batiments, du fabricant de couleurs, etc. Paris: Roret, 12 |
| When cakes of white lead are purchased ready prepared, small particles of lead in the metallic state are not unfrequently found, owing to the preparation having been imperfectly executed; and in grinding the colour, this metallic part, becoming divided by the motion of the muller, gives a greenish tint to it. To avoid this inconvenience, if you do not prepare your white lead yourself, be careful to ascertain, as well as you can, in purchasing it, whether it is pure, and select the thinnest cakes. In grinding it, your slab and muller should be perfectly clean; because there is often a little acid moisture in white lead, which renders it very apt to attract any parts that remain of colours previously ground. To obtain white lead of a very fine quality, it is often necessary to grind it several times. |
| Then the removed lead white is ground in cast iron rollers in a wooden, well closed box, [sieved], then ground fine with water in vertical or horizontal granite stones, the pulp put into the upper wide end of conical, non glazed jars of height 5 Zoll 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. |

| Grindering, 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 leadchalk 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 with a copper spoon with a long handle and so much is added, that the “Sarge” is filled. It takes some time, before its contents have sunken down, when it is again filled, until bit by bit a batch, for instance 10 Centner has gone through. A worker can operate 4 to 5 stones, standing besides each other. The material that collects in the “Sarge” of the lower stone is moved forward to the outlet with a shovel more often, where it falls into a smaller vessel. During first grinding it is often necessary to raise the upper stone a little, because the mass is very thick and therefore does not easily flow between and through both stones. When everything has been ground and the ground mass is a thick pulp, the stone is ground clean by rinsing it with water, the hole of the base stone is washed, for which a coarse brush or a scrubber is used, and then the same pulp is ground more finely several times in the same manner with more closely placed stones. It is better, however, and this is most often done, that the raw lead chalk is passed through one stone and that the fine grinding is done in some other set of stones, which are turned simultaneously, so what comes off the first stone is scooped onto the second, from there onto the third and fourth stone and the grinding takes place evenly and uninterrupted. If soft lead white is made, then one can act the same way both with pure lead white and with mixed types until the finishing; but to prevent it from becoming hard, careful washing is inevitable. For rinsing one needs a number of large vessels, the larger, the better. These vessels are filled with water, the ground lead white is added in and shaken very well, which is very difficult, because it does not dissolve easily. Then it is left to settle, until the liquid is clear and can be drained off. This stirring with fresh water, settling and draining is repeated several times. Then the very thick lead white pulp is placed in a filter, then in presses, to remove the water and is then in irregular chunks left to dry in air or in drying stones, depending on the equipment available. |
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 centres 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 drained 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 it is then possible to use them when it is somewhat useful, however not very pure lead white has accumulated inside, and then feeds it again.

Das Vermahlen kann nun, 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 Bleiweißes auf die Mühle, während sich die Steine gewöhnlich so bewegen, daß sie in der Sekunde 1½ - 1 Umdrehung machen. Man schöpft 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, e. B. 10 Centner durchgegossen sind. Ein arbeiter kann 4 bis 5 Steine, die nebeneinander stehen, bedienen. Was in der der Sarge des Bodensteines sich von Gemahlenem ansammelt, wird durch ein Schlauföfchen öfters nach vorn in den Ablauf geschafft, wo es in einen kleineren Ständer fällt. Bei dem ersten Mahlen ist es häufig nötig, den Stein etwas höher zu stellen, denn weil die Masse sehr dick wird, läuft sie nicht gern unter und durch die beiden Steine. Wenn Alles durchgemahlen ist und woraus das Gemahlene einen zären Brei darstellt, so wird der Stein durch Nachspülen von Wasser rein gemahlen, die Bodensteinmarche auch ausgewaschen, wozu man sich eines groben Haarpinsels oder einer Bürste bedient, und nun wird derselbe Brei noch einige Male auf eben dieselbe Weise bei engen gestellten Steinen hineindurch- und feingemahlen. Besser ist es jedoch, und so wird es auch meistens gehalten, dass man den rohen Bleikalk stets einen Stein passieren lassen und das Feinmahlen auf einige andere Gänge, 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 geschafft 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 Fertigmahlen eben so verfahren; aber damit es nich hart werde, ist ein sorgfältiges Auswaschen unumgänglich erforderlich. Zum Auswaschen hat man dann eine Anzahl grosser Ständer nötig, die um so besser, je grösser sie sind. Diese Ständer fällt 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 Auffüren mit frischem Wasser, Absitzenlassen und Abziehen wiederholt man einige Male. Als dann bringt man den sich sehr dick absetzenden Bleiweißbrei in Filter, von da auf Pressen, um das Wasser zu entfernen und dann in unregelmäßigen Stücken 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 Öffnungen der Sarge um die Bodensteinen herausläuft. In diesem Fall ist leicht eine solche Anordnung der Mahlgänge möglich, dass sie um das vertikal stehende Triebrad herum steigen- oder treppenweise aufgestellt sind, so dass dasjenige, was vom ersten Steine abläuft, direkt durch eine Rinne zu dem andern Stein tritt und so zum dritten und vierten und von da in die Abwässerungstunden, worin das Bleiweiß, wie vorhin schon erwähnt, abgewaschen wird. Dies ist die gewöhnliche Anstellung der deutschen Mühle.


63–72 The next dry grinding is, in the majority of cases still effected under vertical zones, rolling upon a horizontal bed. The ground lead is then shovelled into a cylindrical metallic sieve with fine holes, and enclosed in a wooden box. The powdered white lead is collected at the bottom of the box, and the small flattened particles of metallic lead, fall from the lower end of the sieve into a special receiver. The sifted white lead is mixed with water, and thoroughly ground under mill-stones.

[English factories.] The white lead is also deprived, by washing, of certain soluble salts which may injure its purity; moreover the subsequent operation is always effected with the aid of water. IV. The white lead is mixed with water in troughs, so as to form a soft paste which passes successively through several horizontal mill-stones before it is thoroughly comminuted. This wet grinding is absolutely without danger, since the men do not touch the white lead with their hands, but carry it in scoops or ladles. V. In all the works which we have visited, the soft paste of white lead is poured into conical earthenware pots, which are dried in a stove room. The greater part of the water is expelled, and the blocks becoming contracted, are easily removed from the pots. Their thorough drying is finished in another, or the same, stove room. […] VI. The greater part of the white lead in lumps requires to be ground and sifted again before it is ready for sale. This second grinding, in the majority of works, is still done with vertical stones rolling upon a stone bed. The ground stuff is shovelled into the hopper of a cylindrical sieve, enclosed in a wooden box, where the fine white lead falls. That which has not passed through the meshes of the sieve is collected in another box, and ground anew. The sifted white lead is removed from its box, after the dust has subsided, and packed in barrels either by shaking, or by a slight raming.

cont'd.
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, 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.

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...
To prepare white excellent...
Table 2: Historical recipes for processing lead white with vinegar.


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 whiter wash 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.

Wenn man das Bleiweiß zum Malen gebrauchen will, so muß es mit weifsem Weinölig gereinigt werden. Man reibt es demnach auf einem Porphyre, nachdem man es mit diesem Weinölig angefeuchtet hat, so lange, bis es zu einem unfühlbaren Pulver geworden ist. Hierauf wird es zum Abwaschen in ein Gefäß voll Wasser geschütet, welches man eine Zeitlang schüttelt, läßt es eine kurze Zeit die grössten Theilchen zu Boden fallen, und giesset das noch weifgefärbece Wasser in ein anderes Gefäß, und läßt alles Weiße, das noch in dem Wasser ist, zu Boden setzen, worauf man das darüberschüssige Wasser abgiesset. Auf diese Art erhält man ein sehr schönes und feines Weiße, welches von allem entledigt worden, was seiner Weiße Schaden thun und solche verändern könnte. Denn dieses Weiße fällt nur deswegen gern in das grauchliche oder schwärzliche, weil die Bleithelchen, die darinnen sind, entweder nicht genugsam aufgelöst worden, oder doch zum wenigsten bei der geringsten Berührüng der Luft sehr geneigt sind, sich wieder in Blei zu verwandeln. Der Weinölig aber halt dazu, daß diese Bleithelchen 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.

*See Table 1.*


One of my friends has told me of a procedure to obtain a very pure white. I have not had occasion to test it myself, but I have every confidence in its truth and its faithfulness; besides this procedure, which is practised by others, carries with it everything that is required to convince of its effectiveness, being founded on principles that reason can only approve of.

Take, for instance, a livre, more or less, of good Krems white, subject it, in small batches, to a first grinding with water, without too much concern that it becomes very fine; you take it off the stone in the thickness of a strong cream, and you take care that the first batches do not dry, but that they remain a little liquid. To this end you put every batch of colour in a new well glazed pot, or in a faience bowl, or of pipe clay. When all your white is ground and in a rather thick pulp, pour on top of this pulp the amount of a drinking glass of very good distilled white vinegar; you stir and stir it every hour, and this during one day; you take, to stir it, a new pipe, which the acid of the vinegar does not attack. If your vinegar is good and well distilled, it will remove all little strange particles that may be present in the white, in a manner that nothing remains that can damage your colour. This colour thus prepared provides a very perfect white; but you have to take care to remove all the vinegar by repeated washings, and until the water that floats on top of the white (when you have allowed it to settle) has no more acid taste taking it on the tongue.

The white ground again in pure water, at least three times, has a superior quality; used also with gum water to paint in gouache, it is light, very subtle, and does not turn at all on paper, like happens to Kremsnitz white that has not been subjected to this operation.

Leen de mes amis m’a indiqué un procédé pour obtenir du blanc de toute pureté. Je n’ai pas eu l’occasion d’en faire l’essai moi-même, mais j’ai toute confiance dans sa vérisimité et sa bonne foi; d’ailleurs ce procédé, qui est pratiqué par d’autres, porte avec soi tout ce qu’il faut pour convaincre de son efficacité, étant fondé sur des principes que le raisonnement ne peut qu’approuver.

Prenez, je suppose, une livre, plus ou moins, de beau blanc de Crems, faites-lui subir, en petites parties, une première broyée à l’eau, sans vous attacher à ce qu’il soit très-fin; vous le relèverez de dessus la pierre en bouillie de l’épaisseur d’une forte crème, et vous aurez soin que les premières broyées ne sèchent point, mais qu’elles se conservent un peu liquides. Pour cela vous mettrez chaque relevée de couleur dans un pot neuf bien propre, ou d’une grande épaisseur, et vous aurez soin que les premières broyées ne sèchent point, mais qu’elles se conservent un peu liquides. Pour cela vous mettrez chaque relevée de couleur dans un pot neuf bien propre, ou d’une grande épaisseur, et vous aurez soin que les premières broyées ne sèchent point, mais qu’elles se conservent un peu liquides. Pour cela vous mettrez chaque relevée de couleur dans un pot neuf bien propre, ou d’une grande épaisseur, et vous aurez soin que les premières broyées ne sèchent point, mais qu’elles se conservent un peu liquides. You stir and stir it ever hour, and this during one day; you take, to stir it, a new pipe, which the acid of the vinegar does not attack. If your vinegar is good and well distilled, it will remove all little strange particles that may be present in the white, in a manner that nothing remains that can damage your colour. This colour thus prepared provides a very perfect white; but you have to take care to remove all the vinegar by repeated washings, and until the water that floats on top of the white (when you have allowed it to settle) has no more acid taste taking it on the tongue.

The white ground again in pure water, at least three times, has a superior quality; used also with gum water to paint in gouache, it is light, very subtle, and does not turn at all on paper, like happens to Kremsnitz white that has not been subjected to this operation.
Historical descriptions for pigment decanting or other methods of particle size election.

Table 3

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<td>As in the grinding of colours I gave you an instance but in one for the rest, like I shall do for those colours which are to be washed; I will make my instance in red-lead, which you are to Wash in this manner. Put a quantity thereof into a clean earthen dish, and pour thereto fair water, stirring the colour and water together with your hand or otherwise, then let it stand a while, and before it be settled pour off the third part of the water and let it settle. Then pour yet likewise one other third part out of the viall and reserve the last part in the viall still. This water third divided into three parts let stand still till all be settled and the water cleared, then dry it or make the colour being now setted in the bottome dry by evaporating, and then tempering it with gumme use it at your pleasure.</td>
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While the lead white formed in this operation [= of Krems white] has not been allowed to obtain the hardness of that obtained by the Dutch method [= stack process], it is not necessary to grind; one obtains it very well divided by levigation, by means of a very simple installation. It is composed of a large case that contains nine cases or compartments, of decreasing height. One puts in the most raised case the flakes of lead white, separated first from the metal that has not been attacked. One then enters water from a higher reservoir, and one stirs strongly with a rake: the water overflows quickly, runs into the second case, then into the third, and arrives like this successively in the ninth. One understands that the lead white molecules, taken along by the water, are the more thin the more far they have been carried. Which is found in the lower case is thus the first quality white. One emplies the cases into large vats, where the deposit is formed in more or little time: one then collects it, and when it has drained sufficiently, one puts it in earthenware vases, where it dries and takes the shape of square loaves.

Inserting the lead white into a smooth paste, transferred to a glass jar and then granite grinding slab and wine vinegar was added dropwise until 5–6, table 2). Dry, unwashed pigment was transferred to the stack-process lead white and vinegar (Le Pileur d’Apligny 1779: 126). Washing of the carboxylic lead is very [easy] and is very similar to most processes in this category. One typically uses a large wooden vat, normally of a square shape and divided into several sections, whose number differs between 7–9. These sections have the same size, but not the same height, so that the fluid always drains from one into another, from the first, for instance, the second and so on.

The water, which is poured into the first section of the case, moves bit by bit through the others and everywhere it is stirred a little. The water deposits in proportion the lead white it carries with it, and the precipitation of lead white in the last section is the finest. If one has washed lead white in this manner, one puts it into large vessels, where one washes it again, always leaving it in the water. Das Waschen des kohlensauren Bleies ist sehr [einfach] und hat mit den meisten Verfahrungsarten [dieser] Kategorie große [Ähnlichkeit]. Man bedient sich gewöhnlich einer großen hölzernen Kufe, gemeiniglich von viereckiger Gestalt und in mehrere Fächer abgetheilt, [der] Zahl von 7–9 verschieden ist. Diese Fächer sind von gleicher Geräumigkeit, aber von ungleicher Höhe, so daß [die] Flüssigkeit des einen immer in diejenige des andern über läuft, von der ersten, z. B., in die zweite und so [fort]. Das Wasser, welches man in die erste Abtheilung der Kufe schüttet, gelangt nach und nach in alle [andren] und überall wird es ein Wenig versetzt.

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 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. 5).

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

**Table 3** Historical descriptions for pigment decanting or other methods of particle size election cont’d.


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**Figure 6** SEM BSE image of paint made with lead white and chalk, water washed, paint prepared with poppy oil. False colour image with all lead counts in red, and all calcium counts in green: (a) first ground with water, and (b) first ground with vinegar (See Plate 41 in the colour plate section.)
To prepare... 

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.\(^1\) 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.\(^1\) 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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