'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 (PbCO₃) and hydrocerussite (2PbCO₃·Pb(OH)₂); other lead salts such as plumboanalbite (Pb₅O(OH)₃(CO₃)₂) 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.
To prepare white excellent

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, let it settle 2 or 3 hours Which done, tast the water and when it has dried it must again be humified a little and ground and leave it to bleach and dry up to 5 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. 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 humidy 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.

To wash a whole stoke-process lead white. Historically recipes for washing stack-process lead white.

Table 1

<table>
<thead>
<tr>
<th>Text</th>
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<tbody>
<tr>
<td>Pomaro, G. 1500–1600. I ricettari del fondo palatino della bibliotheca 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. Ad conciare la biacca sottolisima con aqua. Prima macinerai la biacca sottolisima con aqua; poi la lava 3 o 4 volte et lasci lassa secchare in su la pietra, et poi la tolle et serba in una carta.</td>
</tr>
<tr>
<td>Andriessen 1552. Viervoudig tractaetboeck. 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 humidy 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. Looiwit wrytmten op een harden steen met schoon water ende wilmont schoon hebben so als alst wel ghwreven is laatmen uits ghespreyt liggen op die harde wrijfstenen en besprengent met schoon water ende latent soo liggen ende bleken in die heete son ende alst drooghe is salment weder vochtich maecn en op den steen ende wrijvent een poes ende laestend wederom drogen ende bleken tot vier oft vijf reysen toe. Dat is tschoonste wit datmen kav ghwrijvent behouden dat ghie eerst wel uit geseten hebben blauwe loot datter in vals int wrijven dat moutmen allzij wel waz nemen ende uit doen oft dat Looiwit souder worckelijck 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 from the mould, &amp; put it in a straw which will make fine biacca. dappo lo pestate, &amp; lo mettete in un pignatto, &amp; per ogni libra di questo fiore (= lead white), mettete once d'acqua, &amp; ponete al fuoco stermperandolo bene insieme, lo farrete stare tanto al fuoco che levi il fumo, poi cavaleto dal fuoco, &amp; mettete la nella forma che volete, &amp; ponete poi al sole, lassandovelo fin che sia beniasciuto, Finalmente lo truete dalla forma, &amp; mettetela nella paglia che farà Bicca fina.</td>
</tr>
<tr>
<td>Biacca cersse, 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 tin made.</td>
</tr>
<tr>
<td>Veen, J. van c. 1650. 'De wetenschap ende manieren om alderhande couleuren van say of sayetten te verwen'. The Hague: Royal Library, Ms. 135K44, 119</td>
</tr>
<tr>
<td>Lead white is ground with clean water, if you want it beautiful so it bleach on the grinding stone, strew &amp; sprinkled with clean water in the hot sun and when it has dried it must again be humified a little and ground and leave it to bleach and dry up to 5 times; Loodwit wrijftmen op een zuursteen met schoon water, wilt gij't schoon hebben soo laedt het op een wrijften bleiken, uift gestroijt ende besproeght met schoon water ende leet sonseesijn ende aens,t drogo is salben ,t wederom een weijnig natten ende wrijven en laeter, t wederom bleiken en drogen tot ,t op 5 mael toe;</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 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 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. 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 Grownd, and how to Grind them. In the last Section told you what Colours are to be Grownd, which Washed, and which to be Steeped; it resteth now, to shew you how to Grind those Colours that are to be grownd; 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. 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 a faire 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. cont'd.</td>
</tr>
</tbody>
</table>
### Table 1 Historical recipes for washing stack-process lead white cont'd.

<table>
<thead>
<tr>
<th>Name</th>
<th>Recipe Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beurs, W. 1692</td>
<td><em>De groote waereld in het kleen geschildert.</em> Amsterdam: J. and G. Jansonius van Waesberg, 8</td>
</tr>
<tr>
<td>Maar</td>
<td>Maar is to be ground with pure rain water, on a good stone, but especially with no other water, because no other water is pure enough to use. After this time it will be very white and pure.</td>
</tr>
<tr>
<td>Venetiis</td>
<td>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 pure enough to use. After this time it will be very white and pure.</td>
</tr>
<tr>
<td>Smith, M. 1692</td>
<td>The art of painting according to the theory and practise of the best Italian, French, and German masters. London: Vendue, 71</td>
</tr>
<tr>
<td>Eikelenberg, S.</td>
<td><em>1679–1738. Aantekeningen.</em> Alkmaar: Municipal Archive, Ms. Eikelenberg</td>
</tr>
<tr>
<td>Sprong, U. 1738</td>
<td><em>Kabinet der verf-stoffen.</em> Amsterdam: Jacob Graal, 13–14</td>
</tr>
<tr>
<td>Sprong, U. 1738</td>
<td><em>Kabinet der verf-stoffen.</em> Amsterdam: Jacob Graal, 13–14</td>
</tr>
</tbody>
</table>

**For Deadcolouring you may grind white lead in Lyonsed Oyle.**

**The instruments and Materials used in Painting and the preparing Colours to the pallat: Lead White**

**White Flakes being pick'd and scrape'd must first be ground very fine in water, afterwards Temper'd on the stone with the mullet 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 Lyonsed Oyle.
To prepare white excellent...  

4: 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. 

Doeit de te zamen in een steene vysel, en giet een wyng Water daarop, en stampet de verwe vel 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.


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 veale twee soorten, wier eene Veneetsch, 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 gebruukt wordt, 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 isground on a porphyry 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 wryft dit loodwit op den porphyr steen met een weinig water, en maakt .er een deeg van, dat men in vormen tot kleine spitsvrye broodjen maakt, die men drogen laat om te vervoeren;


About the preparation, use and mixing of white paints.


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. 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 water-force 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 weifßen Farbe. 1 Weißes Bleiweiß.

Nachdem das Blei durch die Dämpfe des Eßigs in Bleiweiß zernaget ist, so wird es auf großen Reibesteinen, die als Maschinen in einer großen Fabrik am vortheilhaftesten von dem Wasser getrieben werden können, auf das zarteste gerieben und dabei mit Wasser angefeuchtet, daß ein dicker Brei daraus wiede. Sodenn wird das Bleiweiß in Formen gebildet, die gemeinglich pyramidenförmig sind, und im Sommer an der Luft, im Winter abet 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 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.


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

153: If you want the white lead white really beautiful, you have to grind it with pure water four times on the grinding stone, and as fast as possible. The more one grinds, the more white it becomes. Some grind it first with vinegar, and wash it afterwards with water, because they believe, that the vinegar, through which it was first made, makes it more white; but it is better, to use water right away. If you wish to preserve it after grinding, let it dry in small pieces or grains in a clean place, without dust, and then it can be preserved very well. However if it is intended for oil painting, then mix it, after it has been well ground for four times, with very white poppy oil, by beating the white pulp in order to remove the water and replace it with oil. Then it is ground again very fine, and only a little at a time, preserve it in some glazed jar, and pour a finger high of water on top, in order to preserve the paint, and to prevent a thick skin on top. The preparation with water renders the white lead white more clear and white, compared to, when it is ground straight away with oil. This beautiful white is used for glazes on ordinary lead white. Will man das Schieferweiß recht schön haben, so muß man es viermal auf dem Reibstein mit reinem Wasser, und so hartig als möglich abreiben. Je mehr man reibt, desto weißer wird es. Einige reiben es sogleich mit Essig ab, und waschen es nachher im Wasser, weil sie glauben, der Essig, wodurch es erst entstanden, mache es weißer; es ist aber besser, gleich Wasser zu nennen. Will man es nach dem Abreiben abheben, so läßt man es in kleinen Stücken oder Körnern an einem reinlichen Orte, wo es nicht staucht, trocknen, und kann es alsdem sehr wohl aufbewahren. Ist es hingegen zur Oelmalerei bestimmt, so vernichtet man es, nachdem es zum viertennmal gut abgerieben worden, mit sehr weissen Mohöld, indem man das Weiße immer schlägt, um das Wasser heraus, und das Oel an dessen Stelle zu bringen. Man reibt es alsdem von neuem sehr klar, und nur wenig auf einmal, hebt es in einem in den Boden glasirten Gefäß auf, und gießt einen Finger hoch Wasser darüber, damit die Farbe besser sich halte, und sich keine dicke Haut darüber anlege. Die Zubereitung mit Wasser macht das Schieferweiß reiner und weißer, als wenn man es sogleich mit Oel abreibet. Dieses schöne Weiße wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.

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, 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 fabriceeren van, en den Handel met hetzelve. Het Lood, door den Azyndamp tot Loodwit verkalkt zynde, wordt op grotte wijdistenzen, die by eene Fabriek het voordeeligst werkstukkig door het water gedreven worden, zeer fin gewreven of genalen, en met water tot een ditte brei aangemengd. Vervolgens vormt men het Loodwit in vormen, die doorgaand de gedaante hebben van eenen stompuskerbroedrug; wordende deze broedjes by den zon in de open lucht, en s winters in een tamelijk warm vertrek gedroogd.

Leen, c.1800. Over teken- en schilderkunst & raad aan kunstverzamelaars. [Delfshaven?], 4

To render white, sort whatever, unequall beauty is that ground clean in water, dried and then crushed and ground with fresh poppy oil. Om het wit, welke soort ook, ongemeen schoon te hebben wrijft men hetzelve schoon in water, laat het drogen en dan fijn stoten en met blanke verse papaver of henolie wrijven.


This mill [= mill for grinding lead white] can also be made in small, in this manner: get a large stone and have it caved out in the shape of half a ball, on the upper edge a small channel is carved, through which the mass drips into another jar placed below. Then you have another stone, the shape of half a ball, which exactly fits into the hollow of the first. In the middle of this non-hollowed stone must be a hole, in order to be able to place a funnel, through which the mass is poured in. Through some iron rings, which are secured to the surface of the stone, one sticks a bar, by which a man turns the muller. During grinding you add some water, to make the mass drain off better.

On top of the container, into which the lead white drains from the mill, you place a hair sieve, through which the mass must pass into the container, to retain the coarse materials. When the container is full, you place another one underneath and continue grinding, until all is done. In the containers, in which the lead white runs off, it settles at the bottom, and the water standing on top is removed with taps or holes. Afterwards you pour the lead white on a linen cloth, roughly stretched on a frame, where the [remaining] water drains off. Then it is further dried, either on a tile stove, which one fuels with a small fire, and then applies the mass on top, where it quickly dries; or most commonly like this: one takes planks with holes, in which conically shaped earthenware pots are placed. The hole, which these pots have at the bottom, and through which the water runs out, is closed with paper; the pots are lined with bright blue paper, and then the mass is put in. When the moisture is removed, then the little lead white huts are placed on a wooden board in the air, to dry them completely. Now the lead white is ready for transport. The more the mass is washed with water, the whiter the lead white becomes, and with when adding the finest, whitest and cleanest chalk it also results in the most beautiful lead white. The remaining black deposit consists of unsolved lead, which may be reused for a fresh batch. Diese Mühle [= mill for grinding lead white] kann man auch im kleinen machen, und zwar so: Man läßt einen großen Stein, wie eine halbe Kugel, hohl aushauen, oben am Rande wird eine kleine Rinne eingehauen, durch welche die Masse während des Reibens in ein anderes untergestelltes Gefäß laufen muß. Dieses schöne Weiß wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.

154: If you want the flake white really beautiful, you have to grind it with pure water four times on the grinding stone, and as fast as possible. The more one grinds, the more white it becomes. Some grind it first with vinegar, and wash it afterwards with water, because they believe, that the vinegar, through which it was first made, makes it more white; but it is better, to use water right away. If you wish to preserve it after grinding, let it dry in small pieces or grains in a clean place, without dust, and then it can be preserved very well. However if it is intended for oil painting, then mix it, after it has been well ground for four times, with very white poppy oil, by beating the white pulp in order to remove the water and replace it with oil. Then it is ground again very fine, and only a little at a time, preserve it in some glazed jar, and pour a finger high of water on top, in order to preserve the paint, and to prevent a thick skin on top. The preparation with water renders the white lead white more clear and white, compared to, when it is ground straight away with oil. This beautiful white is used for glazes on ordinary lead white. Will man das Schieferweiß recht schön haben, so muß man es viermal auf dem Reibstein mit reinem Wasser, und so hartig als möglich abreiben. Je mehr man reibt, desto weißer wird es. Einige reiben es sogleich mit Essig ab, und waschen es nachher im Wasser, weil sie glauben, der Essig, wodurch es erst entstanden, mache es weißer; es ist aber besser, gleich Wasser zu nennen. Will man es nach dem Abreiben abheben, so läßt man es in kleinen Stücken oder Körnern an einem reinlichen Orte, wo es nicht staucht, trocknen, und kann es alsdem sehr wohl aufbewahren. Ist es hingegen zur Oelmalerei bestimmt, so vernichtet man es, nachdem es zum viertennmal gut abgerieben worden, mit sehr weissen Mohöld, indem man das Weiße immer schlägt, um das Wasser heraus, und das Oel an dessen Stelle zu bringen. Man reibt es alsdem von neuem sehr klar, und nur wenig auf einmal, hebt es in einem in den Boden glasirten Gefäß auf, und gießt einen Finger hoch Wasser darüber, damit die Farbe besser sich halte, und sich keine dicke Haut darüber anlege. Die Zubereitung mit Wasser macht das Schieferweiß reiner und weißer, als wenn man es sogleich mit Oel abreibet. Dieses schöne Weiße wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.
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...

Een onvergelijkelijke witte loodkleur wordt gemaakt van lood-wit, dat uitgezocht en wel op een' porphiersteen gewreeven 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 afgegoet en hebbende, roer het dan weder door met azijn; herhaal dit nog een of twee maalen, en gij zult een uitspreidend fraai wit, beide voor water- en olieverwen geschikt, bekom en.

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The biacca in the trade to purify, first pulverise, 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 biacca di commercio per depurarla, si usa prima pulverizzarla, e poi sopra gettarvi più d’ una volta dell’acqua bollente; ed a molto necessaria fare questa operazione a quella di Kremnitz, perché contiene uno coll’ animale, donde ripete la sua tenacità.


One clears away the manure, takes out the jars, scraps off the lead white adheres 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 England also in rooms heated by vapour. One does not let them dry completely inside the moulds, because they would be difficult to remove.

Man räumt dann den Mist weg, nimmt die Töpfe heraus, schabt das aus 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 ruhig 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 geschlämmt.

‡) 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 lor 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.

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**) 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 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.

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†) In England 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 reduced or melted. If thin plates are used, they are normally completely corroded.


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

<table>
<thead>
<tr>
<th>Author</th>
<th>Date</th>
<th>Title</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gray, S.F.</td>
<td>1828</td>
<td>The Operative Chemist</td>
<td>London: Hurst, Chance, and Co., 646–7</td>
</tr>
</tbody>
</table>

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.

Vergnaud, A.D. | 1831 | Manuel du peintre en bâtiments, du fabricant de couleurs, etc. | Paris: Roret, 12 |

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.

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 greyish 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.


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Gentele, J.G. | 1860 | Lehrbuch der Farbenfabrikation | Braunschweig: Friedrich Vieweg und Sohn.,159 |

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 leadchalk dough or the dry lead white powder stirred with water is placed on the mill, while the stones are typically in motion, making 1/4-1 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 drains off with the washing water and lead acerate, 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 \textquoteleft Maß\textquotefrighthalf 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 – when it is somewhat useable, however not very pure lead white has accumulated inside, and then feeds it again.

\textbf{VI.} The greater part of the lead white in lumps requires to be ground and sifted again before it is ready for sale. This second grinding, in the majority of cases still effected under vertical zones, rolling upon a horizontal bed. The ground lead is then mixed with 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 – when it is somewhat useable, however not very pure lead white has accumulated inside, and then feeds it again.

\textbf{VII.} 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. […]

\textit{To prepare white excellent…}
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, 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
Historical recipes for processing lead white with vinegar.

**Table 2**

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fortunato of Rovigo 1697 [1659–1711]. 'Raccolta di Secreti,' in M.P. Merrifield, <em>Medieval and Renaissance Treatises on the Arts of Painting</em>. Mineola: Dover (repr. 1980), cli.</td>
<td>To render <em>biacca</em> extraordinarily more white. Take lead white in flakes, choose the most beautiful, and grind well on the marble with vinegar, and</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) stated 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>
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<tbody>
<tr>
<td>(Paulus van Somer) Lead white ground first with water, then washed &amp; allowed to settle, decanting the turbid water, makes a deposit that is very beautiful, &amp; dies less than the deposit.</td>
<td></td>
</tr>
<tr>
<td>King, D. 1632–57. ‘Secrets in the noble arte of miniatura or the art of limning.’ London: British Library, Ms. Additional 12461, 39–40</td>
<td></td>
</tr>
<tr>
<td>Mr. Hilliard's manner of preparing Ceruse. Having ground your ceruse in water without gum &amp; put it into a vial glass with a good quantity of faire water, and being well shaken together, 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 vial and reserve the last part in the vial still. This water third divided into three parts let stand till all be settled and the water cleared, then dry it or make the colour being now setled in the botomme dry by evaporating, Then in tempering it with gummie use it at your pleasure.</td>
<td></td>
</tr>
<tr>
<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 you shall see a filthy greasi scum arise and lie above the water, with other filth; pour this water quite away, and put other clean water to the colour, and stir it about again, pouring away the water (if foul) the second or third time; then add more water, and stir the colour again till the water be thick and troubled; but yet free from filth, then gently pour this troubled water into a second earthen dish, leaving in the first dish all the dregs. Into the second bason put more fair water, and with your hand stir about the colour as before; do thus two or three times, and take (if your colour be very foul) a third earthen dish, and add more water, and keep stirring, till at last the water become clear, and the colour remain fine at the bottom of the dish; pour away your water gently, and you will find some colour remaining and flicking to the edges of the dish, which when it is dry, you may (with a feather) strike away like flower, which reserve as the choicest and purest of all; if in a pound of this red-lead you have an ounce of good indeed, prize it, for it is troublesome to procure. The other, which is not altogether so pure, may be serviceable for some uses, though not for all. What hath been said of this colour is to be understood of all other that are to be washed; therefore for washing of colours let this suffice.</td>
<td></td>
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<tr>
<td>One crushes the flake white in a marble mortar with an iron pestle into a coarse powder. On top of this one pours water, until it becomes a pulp; then grind it further with a stone or glass pestle for some time, until one notices, that it has largely been ground fine. Then a larger amount of water is added, and, after having stirred everything well, let it stand 15 to 20 counts, after which one pours out the liquid with the fine particles that are still retained inside it into a sugar or bowl. The settled more coarse part is ground again and treated in the same manner. And this grinding, pouring on and off is repeated until some blackish, or brown coarse particles remain. The decanted water is left until all the materials have settled; upon which one pours off the superfluous water, and lets the remaining drip through a funnel of blotting paper: finally one dries the remaining pulp between papers. The longer one lets the material settle in the beginning, the more fine the particles will be: but this time is long enough. Anyone who is somehow used to this work can grind as much as a pound of this white very fine in 2 hours. One may without any fear use this manner of fine making for all earthy paint materials.</td>
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<tr>
<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 you shall see a filthy greasi scum arise and lie above the water, with other filth; pour this water quite away, and put other clean water to the colour, and stir it about again, pouring away the water (if foul) the second or third time; then add more water, and stir the colour again till the water be thick and troubled; but yet free from filth, then gently pour this troubled water into a second earthen dish, leaving in the first dish all the dregs. Into the second bason put more fair water, and with your hand stir about the colour as before; do thus two or three times, and take (if your colour be very foul) a third earthen dish, and add more water, and keep stirring, till at last the water become clear, and the colour remain fine at the bottom of the dish; pour away your water gently, and you will find some colour remaining and flicking to the edges of the dish, which when it is dry, you may (with a feather) strike away like flower, which reserve as the choicest and purest of all; if in a pound of this red-lead you have an ounce of good indeed, prize it, for it is troublesome to procure. The other, which is not altogether so pure, may be serviceable for some uses, though not for all. What hath been said of this colour is to be understood of all other that are to be washed; therefore for washing of colours let this suffice.</td>
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<td>One crushes the flake white in a marble mortar with an iron pestle into a coarse powder. On top of this one pours water, until it becomes a pulp; then grind it further with a stone or glass pestle for some time, until one notices, that it has largely been ground fine. Then a larger amount of water is added, and, after having stirred everything well, let it stand 15 to 20 counts, after which one pours out the liquid with the fine particles that are still retained inside it into a sugar or bowl. The settled more coarse part is ground again and treated in the same manner. And this grinding, pouring on and off is repeated until some blackish, or brown coarse particles remain. The decanted water is left until all the materials have settled; upon which one pours off the superfluous water, and lets the remaining drip through a funnel of blotting paper: finally one dries the remaining pulp between papers. The longer one lets the material settle in the beginning, the more fine the particles will be: but this time is long enough. Anyone who is somehow used to this work can grind as much as a pound of this white very fine in 2 hours. One may without any fear use this manner of fine making for all earthy paint materials.</td>
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TO PREPARE WHITE EXCELLENT...
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 sections 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 empires 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. Comme le blanc de plomb formé dans cette opération [= blanc de Krems] n’a pu acquérir la dureté de celui qu’on obtient par la méthode hollandaise [= stack process], il n’est pas nécessaire de broyer; on l’obtient très divisé par le lavage, au moyen d’un appareil extrêmement simple. Il est composé d’une grande caisse contenant neuf cases ou compartiments, de hauteur décroissante. On met dans la case la plus élevée les éclats de blanc de plomb, séparées préalablement du métal qui n’a point été attaqué. On y fait arriver de l’eau d’un réservoir supérieur, et l’on renue fortement avec un rable: l’eau déborde bientôt, s’écoule dans la seconde case, puis dans la troisième, et arrive ainsi successivement dans la neuvième.

On conçoit que les molécules du blanc de plomb, entrainées par l’eau, sont d’autant plus ténues qu’elles ont été charriées plus loin. Ce qui se trouve dans les cases inférieures est donc le blanc de première qualité. On vide les cases dans de grands cuviers, où le dépôt se fait en plus ou moins de temps: on le recueille ensuite, et lorsqu’il est suffisamment épousseté, on le met dans des vases de terre poreux, où il sèche et prend la forme de pains carrés.


Washing of 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, to 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 Wasser, welches man in die erste Abtheilung der Kufe schüttet, gelangt nach und nach in alle [andren] und überall wird es ein Wenig remué fortement avec un rable; l’eau déborde bientôt, s’écoule dans la seconde case, puis dans la troisième, et arrive ainsi successivement dans la neuvième.

De la peinture à l’huile


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 grinding with vinegar would have served to lower the calcium carbonate content in adulterated lead whites. To test this hypothesis, a mixture of lead white and calcium carbonate was ground into a fine, smooth slurry with either distilled water or with vinegar then subsequently water-washed to remove any trace of vinegar. Contrary to expectations, XRD did not indicate a significant shift in calcium carbonate content and
the SEM 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.\textsuperscript{14} 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.\textsuperscript{15} 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 \textit{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).

\section*{Acknowledgements}

The authors thank the Dutch Organisation for Scientific Research (NWO) for sponsoring the HART project; Jef Seynaeve for providing stack-process lead white; Katrien Keune for analysis of the HART samples; Andreas Bilo for assistance with colour measurements; Jaap Boon, Elke Oberthaler and the Reproductions Department of the Kunsthistorisches Museum in Vienna for permission to use the image of the Vermeer cross-section; and Sigrid Eyb-Green and Emilie Froment for checking translations of the recipes.

\begin{notes}
\item 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).
\item 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.
\item HART project (2002–2006), led by Leslie Carlyle, within the de Mayerne Programme, sponsored by the Dutch Organisation for Scientific Research (NWO). Doctoral research by Stols-Witlox on the subject of historical recipes for preparatory layers for oil paintings in northwest Europe, 1400–1900, University of Amsterdam.
\item Produced by Jef Seynaeve, Belgium, for the HART project.
\item 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).
\item 50 ml of vinegar culture (Brouvland 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).
\item Poppy oil produced by the HART project; see Carlyle (2006) for details.
\item 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
\end{notes}
References


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