‘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 plumboacrite (Pb₅O(OH)₂(CO₃)₃) may...
also be found on occasion. \(^1\) Cerussite and hydrocerussite are in chemical equilibrium, which means that depending on the circumstances they can be converted into each other (Godelitissas 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). \(^2\) 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. \(^3\) 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, \(^4\) thoroughly washed with distilled water. \(^5\) Vinegar for grinding with the lead white was prepared from organic, sulphite-free red wine and vinegar culture (bacteria). \(^6\) 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.7 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),8 and the oil paints were then analysed in cross-section with SEM-EDX.9 Colour measurements were made on the paint films using a Konica-Minolta spectrophotometer.10

Figure 2 Occurrence over time of recipes specifying different methods for washing and grinding lead white.

Figure 3 Diffractogram with unwashed, water-washed and vinegar-washed lead white. The position of cerussite peaks is indicated with blue vertical lines, the position of hydrocerussite peaks is indicated with red vertical lines. An increase in cerussite proportion is clearly visible in, for instance, the 25.6 position. (See Plate 40 in the colour plate section.)
Table 1 Historical recipes for washing stack-process lead white.

<table>
<thead>
<tr>
<th>Author</th>
<th>Date</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pomaro, G.</td>
<td>1500–1600</td>
<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>Andriessen 1552</td>
<td></td>
<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 humidi ty 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>Birdelli, c.1601</td>
<td></td>
<td>Then pour it, &amp; put in it 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 in 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>Veen, J.</td>
<td>1650</td>
<td>Lead white is ground with clean water, if you want it beautiful so it bleach on the grinding stone, strew and sprinkled with clean water in the hot sun and when it has dried it must again be humidi tyd a little and ground and leave it to bleach and dry up to 5 times; Looc wit wrytmen op een harden steen met schoon waeter ende wilmont schoon hebben so alswit el gheatreven is laeten uit gheespreyt liggen op die harde wriiffstene en bespreynt met schoon waeter ende latent soo liggen ende bleken in die heete son die alst droogh is salmen weder vochtich maeken op den steen ende wrijven een poes ende laestent wederom drogen ende bleken tot vier oft vijf reegen toe. Dat is tschoonste wit datmen kav ghevijnden behouden dat ghie eerst wel ut geselen hebt biauwe loot datter in valt int wrijven dat moesten alzjft wel waer nemen ende uit doen oft dat Looot wit souder werklik af smetten.</td>
</tr>
<tr>
<td>Symonds 1984</td>
<td>1649–51</td>
<td>To prepare white excellent...</td>
</tr>
<tr>
<td>Anon. 1668</td>
<td></td>
<td>Of those Colours that are to be Grown, and how to Grind them. In the last section told you what Colours are to be Grown, which Washed, and which to be Steeped; it resteth now, to shew you how to Grind those Colours that are to be grown; I shall not run over every Colour particularly, but shew you how to grind one Colour, which take as an example for all the rest. For our example in grinding of Colours, let us take the original of Colours, viz. 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 ground, 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 ground, and there let it rest till it be thorough dry, then take it out ans reserve it in papers, and those papers in boxes, for your use.</td>
</tr>
</tbody>
</table>

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

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

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

Daar toe dan kiezen uit de dikste Schalpen, als de beste, die men in zeer schoon en helder water vrijit op een goede keystone, die niet te hard of te glad wezen kan; en alzoo is gevreesen, zet menne op een stuk van een glas, daar op het water uit droogen moet. Als ze na droog genoeg is, vrytmen die in de beste papaver oly, die de Noot-oly, Lijnsaat-oly en andere bekenden overtref; waar na menne in een rein Schulpie of kommekte doets, en er schoonwater op zet, om niet te verdrogen; en dus kaismeere goed houden; om alts, t voogt is, gebruikt te [...]. T Goede ongenomen Lootwit bereiden op de zelve wyze, als het Schulp-wits; doet t is gemakkelijker om vryvend;

Smith, M. 169. The art of painting according to the theory and practise of the best Italian, French, and Germanem masters. London: Vendeij, 71

The instruments and Materials use'd in Painting and the preparing Colours to the pallet; Lead White

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


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

161: Als men verwen wrijven wil zo nieuw eerst wat loot-wit om den steen wat zuyver te maken en aets, t gewreven is zo doets wat indigo bij, want dit wit dan niet neemt genoeg is om alleen te gebruiken, maar na neemt ander loot-wit en die zal zuyver zijn. T wit komt gj wrijven met water, en laeten droogen en temperen met suet olijf of lijn olijf. Loot-wit wrijft met pís of asijn en als gedroogd is en gij die wiltem gebruiken zo temporreert met olij.

390–9: Lead white is ground with clean water; and it leaves it so beautiful that it can spread on the stone after it has been ground and sprinkled with clean water and leave it thus to bleach in the hot sun and if it is dry it will again be humidified and reground for a while and then dried and bleached up to 4 to 5 times this is beautiful white and when you want to use it you will temper it with gum water. Note. If you grind this lead white you have to search and remove the lead which is normally in it or it would be contaminated from the start.

161: Als men verwen wrijven wilt zo neemt eerst wat loot-wit om den steen wat zuyver te maken en aets, t gewreven is zo doets wat indigo bij, want dit wit dan niet zuyver genoeg is om alleen te gebruiken, maar na neemt ander loot-wit en die zal zuyver zijn. T wit komt gj wrijven met water, en laeten droogen en temperen met suet olijf of lijn olijf. Loot-wit wrijft met pis of asijn en als gedroogd is en gij die wiltem gebruiken zo temporreert met olij.


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

For Deadcolouring you may grind white lead in Lynseed Oyle.


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

Ensuite on broie ces écailles sur une pierre dure, comme porphyre, avec le muller et de l’eau claire, & le plus proprement qu’il est possible pour avoir de beau blanc; quelques fois ces écailles sont couvertes d’une matière grise ou jaune qu’il faut ratisser avant que de les broïer, ce qui peut venir des lames de plomp qui n’étoient pas bien nettes par dessus quand on les a enfermées dans le pot. Le blanc de plomp étant bien broïé à l’eau on laisse bien secher, & on le peut garder tant qu’on veut.

Sprong, U. 1738. Kabinet der verf-stoffen. Amsterdam: Jacob Graal, 13–14

Here we will share a nice trick, on how the lead white may be purified, and made to last. Take lead white, grind it thoroughly with water on a stone; spread it in the open air; but take care, that it does not become too dry; grind it again and expose it to the air, keeping it always wet. Continue this 3 to 4 times, and it will be very white and pure.

Wy zullen hier te plaatse noch een fray hantgreepje ter neer stellen, hoe dat ’t loodwit kan gezuivert, en bestendig gemaakt worden. Neemt Loodwit, vryft t ter dege met een water op een steen; Zet t dus uitgestrekt leggend de, in de open lucht; dogh draagt wel zorg, dat t niet droogh en words; vryft, t dan andermaal en steelt t weer in de locht. T zelve gedurig nut houdende. Vervolgt dit tot drie of vier toighten toe, zoo zalt zeer wit en zuiver zijn.


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

Veneditis loof of schlip wit moet sterk met zuyver regenwater, op een goede steen gevreven worden, maar voor al met geen ander water, om dat geen ander water tot alle boven genmelde verwen goet is.
411–12: To make beautiful lead white.
Place it [= the lead white] together in a mortar, and pour on a little water, and pour 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* to maken.
Doet die te zamen in een steene vesel, en get een wyning *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 papp, 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.

<table>
<thead>
<tr>
<th>Lindenbergh, J.F. 1753. Nieuwe verligter. Amsterdam: Steven van Esveldt, 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flake white. Preparation.</td>
</tr>
<tr>
<td>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.</td>
</tr>
</tbody>
</table>

*Schelpwit. Bereiding.*
Hier van zyn volgens veelte twee soorten, wier eene Venetsch, de andere Inlandsch genaamt word; dog ik hebbe nooit meer dan een soort gezien, *i selve is een der hardste stoffen die in de verwen gebruikt worden, men wrydt die sterk met schoon regenwater op een steen, een lange tyd.*

<table>
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<tbody>
<tr>
<td>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.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Buys, E. 1774. <em>Nieuw en Volkomen Woordenboek</em> (10 vols), vol. 6: K-L. Amsterdam: S.J. Baalde, 754</th>
</tr>
</thead>
<tbody>
<tr>
<td>This lead white is ground 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;</td>
</tr>
</tbody>
</table>

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

<table>
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<tbody>
<tr>
<td>About the preparation, use and mixing of white paints.</td>
</tr>
</tbody>
</table>

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

*Van de bereyding, gebruyk en vermenging der witte verwen, Schelpwit. Bereydinge.*
*men wryft het sterk met schoon regenwater op eenen steen, evenen langen tyd*

<table>
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<tbody>
<tr>
<td>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.</td>
</tr>
</tbody>
</table>


| --- |
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 for transport; but then indeed it is always best to substitute the flake white. |

*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.*

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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 for transport; but then indeed it is always best to substitute the flake white. |

*Siebenter Abschnitt. Von der weifen Farbe. 1 Weißes Bleiweiß.*
*Nachdem das Blei durch die Dämpfe des Elijgs in Bleiweiß zernagelt ist, so wird es auf großen Reibesteinen, die als Maschinen in einer großen Fabrik am vordertheilhaftesten von Wasser getrieben werden können, auf das vartzesthe gerieben und dabei mit Wasser angefeuchtet, daß ein dicker Brei daraus daraus. Sedem wird das Bleiweiß in Formen gebildet, die gemeiniglich pyramidenförmig sind, und im Sommer an der Luft, im Winter aber in einer maßig warmen Stube getrocknet werden.*

| --- |
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 for transport; but then indeed it is always best to substitute the flake white. |


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*Contd.*
153. 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 flake 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.


**Table 1**

**Historical recipes for washing stack-process lead white contd.**


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.

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

To render white, sort what, unequal beauty it is ground clean in water, dried and then crushed and ground with fresh poppy oil.

Brodhagen, P. 1802. Anleitung zur Technologie (3 vols), vol. 1, Hamburg: Bachmann und Gundermann, 378–9

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 miller. 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 when adding the finest, whitest and cleanest chalk it also results in the most beautiful lead white. The remaining black deposit consists of undisolved lead, which may be reused for a fresh batch.

This 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 läuft. Dieses schöne Weiß wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.

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

**Economische kundigheden. Over het LOODWIT, het fabriceeren van, en den Handel met hetzelfde.**

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

To render white, sort what, unequal beauty it is ground clean in water, dried and then crushed and ground with fresh poppy oil.

Om het wit, welke soort ook, ongeen schoon te hebben wijfje hem hetzelvye schoon in water, laat het droegen en dan fijn stoten en met blanke verse papaver of heulolie wrijven.

**Brodhagen, P. 1802. Anleitung zur Technologie (3 vols), vol. 1, Hamburg: Bachmann und Gundermann, 378–9**

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 miller. 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 when adding the finest, whitest and cleanest chalk it also results in the most beautiful lead white. The remaining black deposit consists of undisolved lead, which may be reused for a fresh batch.

This 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 läuft. Dieses schöne Weiß wird mit zum Glasieren auf gemeines Bleiweiß gebraucht.

To render white, sort what, unequal beauty it is ground clean in water, dried and then crushed and ground with fresh poppy oil.

Om het wit, welke soort ook, ongeen schoon te hebben wijfje hem hetzelvye schoon in water, laat het droegen en dan fijn stoten en met blanke verse papaver of heulolie wrijven.
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 non-pergolizable white lookdclear is gained of lead-wit, that ugetocht and well on een' poerhieksteen grownen is, to that the 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 afgegoten hebende, roer het dan weder door met azijn; herhaal dit nog een of tweek malen, and gij zult een uitsluitend freiwit wit, beide voor water- en olieveren geschikt, bekom.


One clears away the manure, takes out the jars, scrapes 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 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 reduced or melted. If thin plates are used, they are normally completely corroded.

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

***) This 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 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 raamt dann den Mist weg, nimmt die Töpfe heraus, schubt 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 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 läft es malen 1). Oft wird es zuletzt noch geschlämmt.

1) In Holland geschieht das malen auf drei nebeneinander stehenden und durch Pferde getriebenen Mühlen. Die erste malt grob, die zweite immer feineres Bleiweiß ab. Gutes Schlämmen trägt wesentlich zur Güte des Bleiweißes bei.


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


In about a fortnight the corrosion is finished, and the sheets of white lead are found near 1/4 inch thick, and covered in some places with crystals of sugar of lead. As much as can be got off by a moderate degree of force, is very carefully washed. This washing is esteemed the most delicate part of the whole manufacture; during the progress of it, a white scum appears which is taken off, and a little lead ash 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.


The flat sheets which cover them [= the jars] provide the flakes, which are kept aside to spread in the trade without any extra preparation. The spirals are unrolled, the smallest and most delicate flakes are removed, and ground with water on horizontal stones. One then washes this ceruse; one lets it deposit and drain, until it has reached a convenient consistency; then one fills conical pots, where it takes the shape that we all know. Les lames plates qui les recouvrent fournissent les écailles, que l’on met à part, pour les repandre dans le commerce sans autre préparation. Les spirales sont déroulées, on en retire des écailles plus petites et plus fiables, que l’on broie à l’eau sous les meules horizontales. On lave ensuite cette céruse; on la laisse déposer et égoutter, jusqu’à ce qu’elle soit en bouillie de consistence convenable: alors on en remplit des pots coniques, où elle prend la forme qu’on lui connaît.


White silver. 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. blanc d’argent. Ce blanc dont se servent les peintres de tableaux, n’est qu’un blanc de plomb de première qualité, que l’on prépare avec le plus grand soin, et que l’on débarrasse, par un grand nombre de lavages, de toute espèce d’impureté.


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.


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. Darauf wird das abgelöste Bleiweiß zwischen gusseisernen Walzen in einem hüllernen, dicht verschlossenen Kasten zermahlen, [gezehrt], sodann unter vertikal oder horizontalen Granitsteinen mit wasser fein gemahlen, [der] Brei in conische, nicht glasierte Töpfe von 5 Zoll Höhe und 3½ Zoll Durchmesser am oberen weiten Theile gethan, welche auf einem Trocknergestelle stehen und täglich einige Male gerühret werden, um die Ablösung des Bleiweiß brodes von der Form zu bewirken. Nach 3 bis 4 Tagen wird die Form umgekehrt und das Brod im Sommer in warmer Luft, im Winter und bei feuchtem Wetter in einer mit warmer Luft geheizten Trockenkammer getrocknet. Zuletzt schlägt man das Bleiweiß in blasser papier ein.


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 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 shovell 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 simultaneouly, 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 acrate, and is too dilute to be further usable. This loss can amount to some percentages. 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 carbosilic 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 carbosilic 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 makes when it is somewhat useable, however not very pure lead white has accumulated inside, and then feeds it again.

Das Vermahlen kann man, wie schon gesagt, auf zweierlei Weise vor sich gehen, je nachdem hartes oder weiches Bleiweiß dargestellt werden soll. Wird hartes dargestellt, so kommt der Teig des Bleikalks oder das mit Wasser angereihterte trockene Pulver des Bleiweisß auf die Mühle, während sich die Steine gewöhnlich so bewegen, daß sie in der Secunde 1 ½ - 1 Umdrehung machen. Man schüttet den Brei mit Hilfe eines langgestielten kugelförmigen Löffels in die kleine Sarge des Läufers und gibt so viel auf, bis die Sarge voll ist. Es dauert dann einige Zeit, bis deren Inhalt niedergesunken ist, worauf man wieder nachfüllt, bis nach und nach eine Partie, z. B. 10 Centner durchgegangen sind. Ein arbeiter kann 4 bis 5 Steine, die neben einander stehen, bedienen. Was in der der Sarge des Bodensteines sich von Gemahlenem ansammelt, wird durch ein Schluffeichen öffers 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 sich sehr unter und durch die beiden Steine. Wenn Alles durchgemahlen ist und wun das Gemahlenem einen zären Brei darstellt, so wird der Stein durch Nachspülen von Wasser rein gemahlen, die Bodensteinmarge 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 enger gestellten Steinen hin und her gemahlen. Besser ist es jedoch, und so wird es auch meistens gehalten, daß man den rohen Bleikalk stets einen Stein passiren lässt und das Feinmahlen auf einigen anderen Gängen, die zu gleicher Zeit in Bewegung sind, ausgeführt wird, dann wird dasjenige, was vom ersten Steine kommt, auf den zweiten, von da auf den dritten und vierten Stein geschöpft und das Mahlen geht dann regelmässig und ununterbrochen fort.

Soll weiches Bleiweiß dargestellt werden, so kann man zwar sowohl bei reinem Bleiweiß, als den gemischten Sorten bis zum Fertigmahlen eben so verfahren; aber damit es nicht hart werde, ist ein sorgfäliges Auswaschen unumgänglich erforderlich. Zum Auswachsen hat man dann eine Anzahl grosser Ständer nötig, die um so mehr, je gruser die Masse ist. 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 läst. Dieses Aufspüren mit frischem Wasser, Abisentenlassen und Abziehen wiederholt man einige Male. Alsdann bringt man den sich sehr dick absetzenden Bleiweisbrei in Filter, von da auf Pressen, um das Wasser zu entfernen und dann in ungereinigten 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 vertikale stehende Triebrad herum stufen- 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 Abwasserungstanden, worin das Bleiweiß, wie vorhin schon erwähnt, abgewaschen wird. Dies ist die gewöhnliche Aufstellung der deutschen Mühlen.


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 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. The white lead, thus ground, is then passed through a vertical millstone, the upper of the pair, to which it is supplied from below, and the ground lead is then passed through a second vertical mill-stone, the lower of the pair, and the lead is then carried 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 ramming.
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

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

78–85: The French or Clichy Process, by Thénard

The settled carbonate of lead is first washed with a small proportion of water, which is added to the decanted solution of acetate. The washing is then continued with larger quantities of water, which are thrown away, since they are too poor in acetate. The paste of white lead is put into pots, and dried in the stove room.

... After a certain length of time, the settling tank is sufficiently filled with white lead, that is, when this material reaches the level of the overflow. The solution is then made to pass into other vessels and the white lead is washed in washing tanks, which are provided with wooden horizontal stirrers having a rotary motion. The settled white lead is covered with twice its volume of pure water and stirred. Three washings take place, and at each, the material is allowed to deposit, and the water above is decanted. The white lead is then conducted into large basins built of porous stones, which absorb part of its dampness. After a few days, the material is divided into blocks which are still quite wet, and which are pounded by wooden vertical stamps falling into a wooden trough inclined from the front backwards.

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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
Table 2  **Historical recipes for processing lead white with vinegar.**

<table>
<thead>
<tr>
<th>Source</th>
<th>Recipe Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fortunato of Rovigo 1607 [1659–1711]. Raccolta di Secreiti, in M.P.</td>
<td>To render biacca extraordinarily more white. Take lead white in flakes, choose the most beautiful, and</td>
</tr>
<tr>
<td>Merrifield, Medieval and Renaissance Treatises on the Arts of</td>
<td>grind well on the marble with vinegar, and it will become black; then take an earthenware beaker full</td>
</tr>
<tr>
<td>Painting: Mineola: Dover (repr. 1980), cl.</td>
<td>of water, and wash your white well, then let it settle well at the bottom, and pour off the water by</td>
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<td></td>
<td>inclination. Return to grinding with vinegar and wash; and having done this approximately 3 or 4 times,</td>
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<tr>
<td></td>
<td>you will have a biacca that will be perfectly beautiful for miniature painting, as well as for oil</td>
</tr>
<tr>
<td></td>
<td>painting.</td>
</tr>
<tr>
<td>Eikelenberg, S. 1679–1738. Aanteekeningen: Alkmaar: Municipal</td>
<td>If you want to grind paints then first take some lead white to clean the stone and when it has been</td>
</tr>
<tr>
<td>Archief, Mss. Eikelenberg, 390–94, 161</td>
<td>ground add some indigo, because this white is not pure enough to use, after this take lead white and it</td>
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<tr>
<td></td>
<td>will be pure. The white you can grind with water, and let dry and temper with nut oil or linsed oil.</td>
</tr>
<tr>
<td></td>
<td>Lead white is ground with urine or vinegar and when dry and you want to use it temper it with oil.</td>
</tr>
<tr>
<td>d’Emery 1709. Nouveau recueil de secrets et curiosites. Amsterdam:</td>
<td>Alimen verwen vrijen wil zo neemt eerst wat loot-wit om den steen wat zuyver te maken en als ’t</td>
</tr>
<tr>
<td>Estienne Roger, 134–5</td>
<td>gewreven is zo doetter wat indigo bij, want dit wit dan niet zuyver genoeg is om alleen te gebruiken,</td>
</tr>
<tr>
<td></td>
<td>maar nu neemt ander loot-wit en die zal zuyver zijn. It wit kort vrijen met water, en laeten droogen</td>
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<tr>
<td></td>
<td>en temperen met noet olj of lijn olj. Looit-wit vrijen met pis of asijn en alse gedroogt is en gij die</td>
</tr>
<tr>
<td>Barrow, J. 1735. Dictionarium polygraphicum (2 vols), vol. 2.</td>
<td>werden vrijen met zuur en de water voorbeelden.</td>
</tr>
<tr>
<td>London: C. Hitch, C. Davis, S. Austen (n.p.)</td>
<td>You have to purify it with white vinegar: so it is ground on a porphyry, while wetting it with vinegar,</td>
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<td></td>
<td>until it is an impalpable powder: then one places it for washing in a vase filled with water, which one</td>
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<td>shakes for some time: one lets settle the largest particles, then one transfers the white water to</td>
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<td></td>
<td>another vessel: one lets precipitate the white, &amp; then one decants the water that floats on top. One</td>
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<td></td>
<td>obtains by this method a very beautiful and very fine white, cleansed of anything that might change its</td>
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<td></td>
<td>whiteness: the reason is that this white is not subject to darkening because of the badly dissolved</td>
</tr>
<tr>
<td>Le Pileur d’Apligny 1779. Traité des couleurs matérielles, Paris:</td>
<td>lead particles that it contains, or at least very disposed to altering itself by the least contact</td>
</tr>
<tr>
<td>Saugrain &amp; Lamy [repr. 1773, Geneva, Minkoff], 5–6</td>
<td>with the air; the vinegar achieves the complete dissolution of these particles, much better than a mineral</td>
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<tr>
<td></td>
<td>acid, because it does not contain phlogistique; at least also developed: it is good for this reason</td>
</tr>
<tr>
<td></td>
<td>only to purify the amount that you need.</td>
</tr>
<tr>
<td>Le Pileur d’Apligny 1779. Traité des couleurs matérielles, Paris:</td>
<td>Lorsqu’on veut employer la céruse en peinture, il faut la purifier avec du vinaigre blanc: on la broie</td>
</tr>
<tr>
<td>Saugrain &amp; Lamy [repr. 1773, Geneva, Minkoff], 5–6</td>
<td>donc sur un porphyre, en l’arrosoyant de ce vinaigre, jusqu’à ce qu’elle soit en poudre impalpable: on</td>
</tr>
<tr>
<td></td>
<td>met ensuite pour la laver dans un vaisseau plein d’eau, qu’on agite quelque temps: on laisse précipiter</td>
</tr>
<tr>
<td></td>
<td>le blanc, &amp; ensuite on le decante le liquide qui flotte.</td>
</tr>
<tr>
<td>Buc hoà, M. 1786. Receuil de secrets sur et expérimentés à l’usage</td>
<td>Or choose the most beautiful lead white in flakes, very white &amp; very soft; grind it on a stone with</td>
</tr>
<tr>
<td>des artistes (no. of vols not known), vol. 3. Paris: by the author,</td>
<td>vinegar, it will become black; but when you have washed it in very clear water, let it settle well,</td>
</tr>
<tr>
<td>291–2</td>
<td>pour off the water by inclination, then grind again with vinegar, &amp; wash again; repeat the same four</td>
</tr>
<tr>
<td></td>
<td>to five times; it will become very beautiful &amp; very bright: it is very good for illumination &amp; for</td>
</tr>
<tr>
<td></td>
<td>painting in oil.</td>
</tr>
</tbody>
</table>

To prepare white excellent...
**Table 2** Historical recipes for processing lead white with vinegar. cont’d.

<table>
<thead>
<tr>
<th>Recipe Description</th>
<th>Reference</th>
</tr>
</thead>
</table>
| **152:** When one uses lead white for painting, it must be cleaned with white wine vinegar. For this purpose one grinds it on a porphyry, after having moistened it with this wine vinegar, until it has become an impalpable powder. Then it is poured into a vessel filled with water for washing, which is shaken for a while, then the coarsest particles are left to settle at the bottom; after that the still whitish water is poured into another vessel, and the white, which is still in the water, is left to settle at the bottom, after which one decants the supernatant water. In this manner one obtains a very beautiful and fine white, which above all has been cleaned of anything, which may harm its whiteness and may change it. Because this white only tends towards grey or black, because the lead particles which remain inside either have not been dissolved completely, or have the tendency to change back into lead upon the least contact with air. The wine vinegar however helps to dissolve these lead particles completely, and even better than any mineral acid would, because this does not have an inflammable nature, at least not openly. When man das Bleiweiß zum Malen gebrauchen will, so muß es mit weißem Weinigef gereinigt werden. Man reibt es demnach auf einem Porphyrstein, nachdem man es mit diesem Weinigef angefeuchtet hat, so lange, bis es zu einem unlöslichen Pulver geworden ist. Hierauf wird es zum Abwaschen in ein Gefäß voll Wasser gesetzt, welches man eine Zeitlang schüttelt, läßt es eine kurze Zeit die grüngrüten Theilchen zu Boden fallen, und giesset das noch weißgefärbte Wasser in ein anderes Gefäß, und läßt alles Weiß, das noch in dem Wasser ist, zu Boden setzen, worauf man das darüberstehende Wasser abgiesset. Auf diese Art erhält man ein sehr schönes und feines Weiß, welches von allem entledigt worden ist, was seiner Weißigkeit Schaden thun und solche verändern könnte. Denn dieses Weiß fällt nur deswegen gern in das graulichte oder schwärzliche, weil die Bleithelchen, die darinnen sind, entweder nicht genugsaum aufgelöst worden, oder doch zum wenigsten bei der geringsten Berührung der Luft sehr gezeugt sind, sich wieder in Blei zu verwandeln. Der Weinigef aber hält dazu, daß diese Bleithelchnen 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.

---

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
Historical descriptions for pigment decanting or other methods of particle size election.

**Table 3**

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Paulus van Somer)</td>
<td>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.</td>
<td>1623–57</td>
<td><em>Secrets in the noble arte of miniatura or the art of limning</em> London: British Library, Ms. Additional 12461, 39–40</td>
</tr>
<tr>
<td>Mr. Hillards manner of preparing Ceruse.</td>
<td>Having ground your ceruse in water without gum &amp; put it into a viall glass with a good quantity of faire water, and being well shaken together, let it stand a while, and before it be settled poure off the third part of the water and let it settle. Then poure 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 botteme dry by evaporating. Then in tempering it with gumme 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.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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 grosse 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 about 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 flitting 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. |

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 somewhat 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 fine manner of making for all earthy paint materials. |

Men stoot het schulpwit in een maarmere mortier met een yzere stamper tot een grof poeyer. Hier op giet men water, tot het een pap werde: dan wryft men verders met een steene of glaaze stamper eenigen tyd lang, tot men bemerkt, dat er een goed deel fyn gewreven is. Hier op giet men er verder met een ruime hoeveelheid waater, en, naa alles wel omgeroerd te hebben, laat men ’t 15 à 20 tellen staan, waarna men ’t degit van de daar noch in opgehouden worckende fyn deeltjes in een zuiker glas of kom overget. Het gezakte groeven deel wort wederom gewreven, en op dezelfde wyze behandeld. En dit wryven, op- en afgieten herhaald men zo lang tot er eenige zwartagtige, of bruine groove deeltjes te rug blyven. Het afgegootene water laat men staan tot alle stoffe geraakt zy; wanneer men ’t overvloedige water er afgiet, en ’t overige door een tregter van lek papier er laat uitdraipen: eindelyk droogt men de overgeblevene pap tuschen papieren. Hoe langer men in den beginne de stof laat zakken, dies te fynder zyllen de deeltjes zyn: doch deze bepaalde tyd is lang genoeg. Die eigensyn aan deze behandeling gewend is kan in 2 waren tyds wel een pond van dit wit fijn wryven. Men mag zonder enige vreeze deze wyze van fynmakking by alle aardagtye verstoffen in, ’t werk stellen.


**See Table 2.**

Anon. (A.P.S.) | 1770 | *Nauwkeurige beschryving van het schilderen der zwarte konstprinten. Groningen: Broekema, 27 |

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 somewhat 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 fine manner of making for all earthy paint materials. |

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**See Table 2.**


**See Table 2.**


Method to wash raw colours. The traders or manufacturers of pigments wash them in large cases or wooden jars, in which there may enter hundreds. They use two taps, at different heights, to first let run off the first waters, on which float all the light materials; then another, lower down, to separate the good colour from the sediment, which is filled with stones and other heavy materials. |

**Manière de laver les Couleurs brutes.** Les marchands ou fabricans de couleurs les lavent dans de grandes caisses ou jarres de bois, où il en peut entrer des centaines. Ils pratiquent deux robinets, à différentes hauteurs, pour laisser d'abord écouter les premières eaux, sur lesquelles surnagent tous les corps légers; puis un autre, plus bas, pour séparer la bonne couleur d'avec le sédiment, qui est rempli de pierres et autres corps pesans. 

**cont.**
Table 3 Historical descriptions for pigment decanting or other methods of particle size evaluation continued.


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 empies 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.

As the blanc de plomb formed in this operation [= of Krems] rida 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 la levigation, 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 éclatés de blanc de plomb, séparés 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 bientot, 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, entraînées 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 égoutté, 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.


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.)

stack-process lead white and vinegar (Le Pileur d’Apligny 1779: 5–6, table 2). Dry, unwashed pigment was transferred to the granite grinding slab and wine vinegar was added dropwise until the consistency of double cream was reached. The paint was ground into a smooth paste, transferred to a glass jar and then washed eight times with distilled water to remove all traces of vinegar. No pigment discoloration as mentioned by Fortunato was noted between both washing methods, grinding in vinegar did result in compositional changes. These became evident when the differently treated pigments were analysed by XRD. Comparison of XRD results of untreated lead white, lead white ground with water and that ground with vinegar showed that water washing raised the proportion of cerussite by removing the other forms of lead salts, while washing with vinegar resulted in an even higher concentration of cerussite (Fig. 3). Although no strong difference in the resulting particle sizes or shapes could be noted between both washing methods, grinding in vinegar did seem to result in a slightly raised proportion of small particles as compared to clumps of aggregated particles (Fig. 4a and b).

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
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.12 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.13 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).

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.
References


Mulder, G.J. 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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References


