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

Stols-Witlox, M.; Megens, L.; Carlyle, L.

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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 (PbCO$_3$) and hydrocerussite (2PbCO$_3$.Pb(OH)$_2$); other lead salts such as plumbonacrite (Pb5O(OH)2(CO3)$_3$) may
also be found on occasion. Cerussite and hydrocerussite are in chemical equilibrium, which means that depending on the circumstances they can be converted into each other (Godelitsas et al. 2003), therefore the presence and ratio of lead salts in a given pigment sample will depend on variables during the production process – such as the location of the ceramic container within the stack itself and the quality of the starting materials (Homburg and Vlieger 1996: 39) – or on processing methods. Some reports in the late 19th and early 20th century state that the freshly produced pigment contained some residual lead acetate (Carlyle 2006: 15).

Most studies have confirmed the presence of lead white in paintings by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDX). Although this method detects the presence of the element lead, it does not identify the formulation or quantity of lead salts present in the pigment. Therefore little information on the exact composition of lead whites in paintings is available in the modern technical literature. However, the SEM can provide additional information on lead white. Since SEM backscattered electron (BSE) images show particle morphology, they may be used to obtain an indication of whether or not lead white has been post-processed. This approach was employed successfully in a recent study by Boon and Oberthaler (2010) of The Art of Painting by Johannes Vermeer, dated to the 1660s. SEM BSE images demonstrate that the top layers of whitish passages in the painting contain a lead white with very small particles (possibly denoting a very fine grade of pigment), whereas for the ground and lower paint layers, a much coarser lead white has been employed with a considerably larger range of particle or aggregate sizes (see Fig. 1). Berrie and Matthew have reported similar differences in particle size (2011: 295).

How were different grades of lead white obtained, what was their exact composition and what are the possible consequences of their use for the visual characteristics of the final paint layer and for the way the paint ages? This paper investigates the effects of washing, grinding and decanting methods by reconstructing historical recipes, and analysing the effects of these treatments on pigment morphology and composition.

Materials and methods

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

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

Reconstructions were executed with traditionally prepared stack-process lead white, thoroughly washed with distilled water. Vinegar for grinding with the lead white was prepared from organic, sulphite-free red wine and vinegar culture (bacteria). Lead white pigments, further
processed by grinding with vinegar and/or further water washing, were subsequently made into oil paint by hand grinding with poppy oil extracted from a single seed lot from a single supplier.\textsuperscript{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),\textsuperscript{8} and the oil paints were then analysed in cross-section with SEM-EDX.\textsuperscript{9} Colour measurements were made on the paint films using a Konica-Minolta spectrophotometer.\textsuperscript{10}
Table 1 Historical recipes for washing stack-process lead white.

<table>
<thead>
<tr>
<th>Author</th>
<th>Year</th>
<th>Location</th>
<th>Recipe Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Andriessen</td>
<td>1552</td>
<td>Kampen: Steven Joessen, 55</td>
<td>Lead white is ground on a hard stone with clean water and if you want it fine then when it is well ground take it spread on a hard grinding stone and sprinkle on clean water and leave it to bleach in the hot sun and when it is dry humidify it again on the stone and grind it for a while and let it dry again and bleach, so long as there are up to four or five times. This is the most clean white that you can find if you dust off the blue lead that falls in during grinding that must always be removed or the lead white would truly stain. Looitwit wrijftmen met schoon water ende wilment schoon hebben so alst wet ghewreen is laten uit ghenspreyt liggen op die harde wrijfsteen en besprengent met schoon water ende latent soo liggen ende bleken in die heete son ende alst drooghe is salment weder vochtich maecchen op den steen ende wrijvent een poes ende laatst wederom drogen ende bleken tot vier oft vijf reysen toe. Dat is tochoonste wit datmen kan ghewijndern behouden dat ghie eerst vel uit gelesen hebt btlauwe loot datter in valt int wrijven dat moesten alzijt wel waer nemen ende uit doen oft dat Looitwit souder werschelijck af smetten.</td>
</tr>
<tr>
<td>Birelli</td>
<td>c.1601</td>
<td>Milan: Giorgio Maroscotti, 363</td>
<td>Then grind 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 it from the mould, &amp; put it in straw which will make fine biacca. Doppo lo pestate, &amp; lo mettete in un pignattto, &amp; per ogni libra di questo fiore [= lead white], mettete oncie due d'acqua; &amp; ponetelo al fuoco stemperandolo bene insieme, lo farrete starn tanto al fuoco che levi il fumo, poi cavatelo dal fuoco, &amp; mettetela nella forma che volete, &amp; ponetelo poi al sole, lasciandovelo fin che sia beniscuitato, Finalmente lo truete dalla forma, &amp; mettetela nella paglia che farà biacca fina.</td>
</tr>
<tr>
<td>Pomaro</td>
<td>1500–1600</td>
<td>Milan: Giunta Regionale Toscana Editrice Bibliografica, 98 (Pal. 796: c. 5v)</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. Ad conciare la biacca sottissima con acqua. Prima macinerai la biacca sottissima con acqua; poi la lava 3 o 4 volte e lasciala secchere in su la pietra, et poi la tolle et serba in una carta.</td>
</tr>
<tr>
<td>Veen</td>
<td>1650</td>
<td>London/New York: Garland, 225</td>
<td>Biacca cersue, white. When S. G. A. was to finish the quadro of Cleopatra A. M. ground Biacca that is whyting wht water very well, then to take out the water ground it in Olio di lino washing it often, pouring on water constantly: This was to purify the Biacca &amp; take out all the lead of wht tis made.</td>
</tr>
<tr>
<td>Symonds</td>
<td>1649–51</td>
<td>London: British Library, Ms. Additional 12461, 38–9</td>
<td>To prepare white excellent To 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 clean water and let it dry again and bleach that falls in during grinding that must always be removed or the lead white would truly stain. Looitwit wrijftmen met schoon water, wilt gi't schoon hebben soo laedt het op een wrijfsteen bleikchen, uijt gestrojyt ende besproyt met schoon water inde heete sonneschijn ende eeuens, t droog is salmen, t wederom een weijnig natten ende wrijven en laetste, t wederom bleiken en droogen tot t op 5 mael toe;</td>
</tr>
<tr>
<td>Andriessen, Anon.</td>
<td>1552</td>
<td>Kampen: Steven Joessen, 55</td>
<td>Lead white is ground on a hard stone with clean water and if you want it fine then when it is well ground take it spread on a hard grinding stone and sprinkle on clean water and leave it to bleach in the hot sun and when it is dry humidify it again on the stone and grind it for a while and let it dry again and bleach, so long as there are up to four or five times. This is the most clean white that you can find if you dust off the blue lead that falls in during grinding that must always be removed or the lead white would truly stain. Looitwit wrijftmen met schoon water ende wilment schoon hebben so alst wet ghewreen is laten uit ghenspreyt liggen op die harde wrijfsteen en besprengent met schoon water ende latent soo liggen ende bleken in die heete son ende alst drooghe is salment weder vochtich maecchen op den steen ende wrijvent een poes ende laatst wederom drogen ende bleken tot vier oft vijf reysen toe. Dat is tochoonste wit datmen kan ghewijndern behouden dat ghie eerst vel uit gelesen hebt btlauwe loot datter in valt int wrijven dat moesten alzijt wel waer nemen ende uit doen oft dat Looitwit souder werschelijck af smetten.</td>
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*TO PREPARE WHITE EXCELLENT...*
Table 1  Historical recipes for washing stack-process lead white

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<thead>
<tr>
<th>Author</th>
<th>Date</th>
<th>Recipe Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pictorius, J.</td>
<td>1747</td>
<td>Lead white is 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.</td>
</tr>
<tr>
<td>Sprong, U.</td>
<td>1738</td>
<td>For Deadcolouring you may grind white lead in Linseed Oil.</td>
</tr>
<tr>
<td>Hyre, P. de la</td>
<td>1730</td>
<td>For Deadcolouring you may grind white lead in Linseed Oil.</td>
</tr>
</tbody>
</table>

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: Almen verwen wijfjen wil zo noten eerst woat loot-wit om de steen wat zayer te maken en als, t gewezen is zo doeter wat indigo bij, want dit wit dan niet zayer genoeg is om alleen te gebruiken, daer na noten ander loot-wit en die zal zayer zijn. Dit wit kon gij wijfjen met water, en laeten droogen en tempenent met suet olijf of lijn olijf. Loot-wit wijf met pis of asijn en alle gedrooven is en gij die wilt gebruiken zo tempertse met olijf.

390–94: Lead white is ground with clean water; 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 Dead Colouring you may grind lead white in Linseed Oil. 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 Dead Colouring you may grind white lead in Linseed Oil. 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.
411–12: To make beautiful lead white.
Place it (= the lead white) together in a mortar, and pour on a little water, and pound the paint for as much as half an hour, (it is better with water on a mill, such as potters use for their glazes) until it becomes as pulp, then put the paint with a spoon in one or two pots, and put it in the sun, and let it become hard, then it is ready.

Schoon Loot Wit to make.

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

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

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

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


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

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

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

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


About the preparation, use and mixing of white paints.
Flake white. Preparation. It is ground vigorously with clean rain water on a stone, a long time.

men wryft het sterk met schoon regenwater op eenen steen, eene 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 waterforce like machines, as tenderly as possible and humidified with water, so a thick pulp results. Then the lead white is cast in moulds, which are normally pyramid shaped, and dried in summer in the open air, in winter however in a moderately warm oven.

Siebenter Abschnitt. Von der weißen Farbe. 1 Weiße Bleiweiße. Nachdem das Blei durch die Dämpfe des Eßigs in Bleiweiß zernaget ist, so wird es auf grossen Reibesteine, die als Maschinen in einer großen Fabrik am vortheilhaftesten vom Wasser getrieben werden könnhen, auf das zarteste gerieben und dabei mit Wasser angefeuchtet, daß ein dicker Brei daraus wird. So wird das Bleiweiß in Formen gebildet, die gemeinnützig pyramidenförmig sind, und im Sommer an der Luft, im Winter aber in einer mäßig warmen Stube getrocknet werden.

151: The factory grinds the lead white unmixed; however, it most commonly receives on the mill an addition of chalk. The pure flake white is cast in moulds, which are normally pyramid shaped, and dried in summer in the open air, in winter however in a moderately warm oven.


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

*Will man das Schieferweiß recht schön haben, so muß man es viernal auf dem Reibstein mit reinem Wasser, und so hartig als möglich abreiben.*


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

Economical knowledge. About LEAD WHITE, it's 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 kundigteden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelfde.

*Het Lood, door den Azynamp tot Loodwit verkaldt zynde, wordt op grotte wrijftstenen, die by eene Fabrick het voordeeligst werkzaigelijk door het water gedreven worden, zeer fyn gewreven of gemalen, en met water tot een dikke brei aangemengd. Vervolgens vormt men het Loodwit in vormen, die doorgaards de gedaante hebben van een stoomspikerbroodj; wordende deze broordjes by den zomer in de opene lucht, en ’s winters in een taaamlyk warm vertrek gedroogd.*

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

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

Om het wit, welke soort ook, ongemeen schoon te hebben wijft men hetzelfde schoon in water, laat het drogen 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 a 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 unsolved lead, which may be reused for a fresh batch.

Diese Mülle [= mill for grinding lead white] kann man auch im Kleinen machen, und zwar so: Man läßt einen großen Stein, wie eine halbe Kugel, in Rahmen gespannte Leinwand, wo das Wasser vollends abläuft. Dann wird es weiter...

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’ porfiersteen gewreven is, tot dat het zwartachtig wordt. Neem dan een pot vol water, wasch het lood-wit daar wel zuiver in af, en laat het bezinken; en het water er afgegooid hebbende, roer het dan weder door met azijn; herhaal dit nog een of twee maalen, en gij zult een uitsnemend fraai wit, beide voor water- en olieverwen geschikt, bekomen.


The bianca 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 Krennitz [white], because it contains animal glue, from which it obtains its stiffness.

La bianca di commercio per depurarla, si usa prima polverizzarla, e poi sopra gettarvi più d’una volta dell’acqua bollente; ed è molto necessaria fare questa operazione a quella di Krennitz, perchè contiene uno coll’ animale, donde ripete la sua tenacità.


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 renewed 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 froth, which contains much sugar of lead. In order not to lose this, one adds some potash, which decomposes it and creates a deposit of carboxyl 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.

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


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

*) In England auch durch Dampf geheizten Zimmern. Man läßt es in den Formen nicht ganz trocken werden, da es sonst schwer herauszuziehen sein würde.


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

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

cont.
Table 1

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<th>Name</th>
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<th>Reference</th>
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</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 peashell 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 écailltes, 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 fribles, 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 bouillage de consistence convenable: alors on en remplit des pots coniques, où elle prend la forme qu'on lui connaît.

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 which one releases, by a large number of washings, of every possible impurity.

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

Then the removed lead white is ground in cast iron rollers in a wooden, well closed box, [sieve], 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.


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 made, the lead white is wrapped in blue paper. Darauf wird das abgelöste Bleiweiß zwischen gußeisernen Walzen in einem hölzernen, dicht verschlossenen Kasten zermahlen, [gesiebt], sodann unter horizontalen oder verticalen Granitsteinen mit Wasser fein gemahlen, [der] Brei in conische, nicht glasirte Töpfe von 5 Zoll Höhe und 3½ Zoll Durchmesser am obern weiten Theile gethan, welche auf einem Trocknergestell stehen und täglich einige Male gerüttelt 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 blaue papier ein.

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 stoves, 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 percents. To prevent this, one can do two things. One adds to the first water, with which a lead white is stirred, one “Maß” of a crystal soda solution, which results in a precipitation, in which the dissolved lead settles as carboxylic lead oxide. Or – which is the best method – one directs all the draining wash water into a slake, to which an excess of chalk or carboxylic chalk has been added, where the lead then settles bit by bit as lead white and calcium carbonate dissolves in return. After a long time one examines the contents of the slake and empties it when somewhat useable, however not very even white lead 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 Teil des Bleikalks oder das mit Wasser angerührte trockene Pulver des Bleiweißes auf die Mühle, während sich die Steine gewöhnlich so bewegen, daß sie in der Secunde 1½ - 1 Umdrehung machen. Man schöpft den Brei mit Hilfe eines langgestielten kupfernen Löffels in die kleine Sarge des Läufers und gibt so viel auf, bis die Sarge voll ist. Es dauert dann einige Zeit, bis deren Inhalt niedergesenkt ist, worauf man wieder nachfüllt, bis nach und nach eine Partie, z. B. 10 Centner durchgegossen sind. Ein arbeitet kann bis 4 bis 5 Steine, die neben einander stehen, bedienen. Was in der der Sarge des Bodensteines sich von Gemahlenem ansammelt, wird durch ein Schlauchfechen ofters nach vorn in den Ablauf geschafft, wo es in einen kleineren Ständer fällt. Bei dem ersten Mahlen ist es häufig nötig, den Stein etwas höher zu stellen, denn weil die Masse sehr dick wird, läuft sie nicht ganz unter und durch die beiden Steine. Wenn Alles durchgemahlen ist und wann das Gemahlene einen zären Brei darstellt, so wird der Stein durch Nachspülen von Wasser rein gemahlen, die Bodensteinarme auch ausgewaschen, wozu man sich eines groben Haarpinsels oder einer Bürste bedient, und nun wird derselbe Brei noch einige Male auf ebene dieselbe Weise zuerst gemahlen und in den letzteren, wo dann das Blei sich nach und nach auscheidet und kohlensauren Bleioxyd. Oder man läßt, was jedenfalls das beste ist, alle die fallenden Waschwasser in einen Sumpf laufen, worin ein Ueberschuß

63–72 The next dry grinding is, in the majority of cases still effected under vertical zones, rolling upon a horizontal bed. The ground lead is then shovelled into a cylindrical metallic sieve with fine holes, and enclosed in a wooden box. The powdered white lead is collected at the bottom of the box, and the small flattened particles of metallic lead, fall from the lower end of the sieve into a special receiver. The sifted white lead is removed from its box, after the dust has subsided, and packed in barrels either by shaking, or by a


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[English factories:] The white lead is also deprived, by washing, of certain soluble salts which may injure its purity; moreover the subsequent

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

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

The salt mentioned by King most probably consisted of lead acetate. During water washing of lead white carried out by the HART project, lead acetate levels were monitored; after numerous water changes lead acetate was no longer detectable. An overview of water-washing recipes within the period under investigation (Table 1) shows that the main methods used were either washing with large amounts of clean water, repeated grinding with water on the slab, or a combination of both treatments. Comparison of XRD analyses of unwashed and water-washed lead white confirmed the findings of the
To prepare white excellent...
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 lead white that had been cleaned with white wine vinegar. For this purpose one grinds it on a porphyrin, 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 one uses lead white for painting, it must be cleaned with white wine vinegar. For this purpose one grinds it on a porphyrin, 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.

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Table 3 Historical descriptions for pigment decanting or other methods of particle size election.

<table>
<thead>
<tr>
<th>Source</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mayerne, T.T. de 1620–44. <em>Pictoria Sculptoria &amp; quae subalternarum artium.</em> London: British Library, Ms. Sloane 5052, 96v (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. Le blanc de plomb broye premièrement avec eau, puis lavé &amp; laissé rasseruer, en decantant l’eau trouble, fait une résidence qui est tres belle, &amp; meurt moins que le fonds.</td>
</tr>
<tr>
<td>King, D. 1653–57. <em>Secrets in the noble arte of miniatura or the art of limning.</em> London: British Library, Ms. Additional 12461, 39–40</td>
<td>Mr. Hilliards 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 still till all be settled and the water cleared, then dry it or make the colour being now setted in the bottome dry by evaporating. Then in tempering it with gumme use it at your pleasure.</td>
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</table>

**Method to wash raw colours:**

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 greasier scum arise and lie above the water, with other fluid; 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 basin 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.

**Table 3 cont’d.**
While the lead white formed in this operation [= of Krems white] has not been allowed to obtain the hardness of that obtained by the Dutch method [= stack process], it is not necessary to grind; one obtains it very well divided by levigation, by means of a very simple installation. It is composed of a large case that contains nine cases or compartments, of decreasing height. One puts in the most raised case the flakes of lead white, separated first from the metal that has not been attacked. One then enters water from a higher reservoir, and one stirs strongly with a rake: the water overflows quickly, runs into the second case, then into the third, and arrives like this successively in the ninth. One understands that the lead white molecules, taken along by the water, are the more thin the more far they have been carried. Which is found in the lower case is thus the first quality white. One emplies the cases into large vats, where the deposit is formed in more or little time: one then collects it, and when it has drained sufficiently, one puts it in earthenware vases, where it dries and takes the shape of square loaves.

Comme le blanc de plomb formé dans cette opération [= blanc de Krems] n’a pu acquérir la dureté de celui qu’il 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 casiers ou compartiments, de hauteur décroissante. On met dans la case la plus élevée les écailles de blanc de plomb, séparées préalablement du métal qui s’a point été attaqué. On y fait arriver de l’eau d’un réservoir supérieur, et l’on renouvelle fortement avec un râle: 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, 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 séche 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, into 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.


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 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).

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

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

<table>
<thead>
<tr>
<th>Time</th>
<th>Method</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>17/01/2012</td>
<td>SEM BSE</td>
<td>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.)</td>
</tr>
</tbody>
</table>
To prepare the SEM BSE images made from the paints prepared from the test materials do not reveal apparent changes in their visual characteristics (Fig. 6a and b).

**Decanting**

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

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

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

If the XRD results for the dry pigment samples can be used as an indication of the composition of the lead white in paint, they appear to contradict the results of Welcomme et al. (2007), who found a higher ratio of hydrocerussite to cerussite in the paint layers as compared to the ground layers of paintings (dated between 1512 and 1516) by Matthias Grünewald.

Investigation of the change of composition of lead white in paint is ongoing. Yet unpublished results from the HART project appear to show that the ratio of hydrocerussite to cerussite is lower in lead white paint tempered with linseed oil than in the dry pigment powder from which it was prepared. The different observations on the ratio of hydrocerussite to cerussite might also be linked to the equilibrium between the two in water, which can easily shift to either side under ambient conditions (Godelitsas et al. 2003).

**Conclusion and future research**

Our reconstructions of water washing, vinegar grinding and decanting have provided more insight into the effects of these processing methods on visual characteristics of particles within paint cross-sections, as well as on their composition. The question of whether oil paints containing only very fine lead white were created by extensive grinding or by decanting can now be decided in favour of decanting. Our reconstructions have shown all treatments to influence the balance between cerussite and hydrocerussite, all resulting in a higher proportion of cerussite.

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

Are there any benefits to using lead white with a high proportion of cerussite? Colour measurements indicate that after two months of natural ageing, vinegar-treated lead whites have yellowed considerably more than water-washed lead whites.
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).

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**Notes**

1. Plumbonacrite is reported to transform easily to hydrocerussite and is not always detected in lead white samples (Olby 1966). Its presence was analysed with XRD by Hallebeek of the (then) Netherlands Institute for Cultural Heritage in lead white samples analysed for the HART project (Carlyle 2006: 50).
2. Argon ion polishing of lead white oil paint cross-sections (Boon and van der Horst 2008), followed by ultra high magnification with SEM demonstrates that so-called large ‘particles’ of lead white are not solid material but are composed of aggregates of small particles.
4. Produced by Jef Seynaeve, Belgium, for the HART project.
5. Distilled water was added to previously crushed lead white. Pigment and water were stirred for two minutes. After settling of the pigment, supernatant water was poured off and replaced with fresh distilled water 8–10 times. This method closely follows the one used by the HART project (Carlyle 2006: 25–6).
6. 50 ml of vinegar culture (Brouwland of Everlo, Belgium, purchased 18/9/2010) was added to 500 ml sulphite-free organic red wine (Stellar Organics, Shiraz, South Africa, imported from Coenecoop Wine Traders B.V., 2742 RC Waddinxveen). The liquid was allowed to acidify during four weeks in a cool, dark place. The resulting vinegar had a slightly pink colour and a pH of 3–4 (Macherey-Nagel pH-Fix 0–14).
7. Poppoy oil produced by the HART project; see Carlyle (2006) for details.
8. The crystalline phases were analysed by XRD using a Discover D8 microdiffractometer with a general area detection diffraction system (GADDS) two dimensional detector (Bruker AXS, Karlsruhe, Germany). Powdered samples were applied in a little
References


Authors’ addresses

• Maartje Stols-Witlox, University of Amsterdam, Ateliergebouw, Hobemastraat 22, 1071 CZ Amsterdam, The Netherlands. (m.j.n.stols-witlox@uva.nl)
• Luc Megens, Cultural Heritage Agency of the Netherlands, Ateliergebouw, Hobemastraat 22, 1071 CZ Amsterdam, The Netherlands. (l.megens@cultureelgoed.nl)
• Leslie Carlyle, Department of Conservation, Faculty of Sciences and Technology, New University of Lisbon, Caparica Campus, Caparica 2829-516, Portugal. (l.carlyle@btinternet.com)