'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 (PbCO$_3$) and hydrocerussite (2PbCO$_3$.Pb(OH)$_2$); other lead salts such as plumboacmite (Pb5O(OH).3(CO$_3$)$_2$) may...
also be found on occasion. Cerussite and hydrocerussite are in chemical equilibrium, which means that depending on the circumstances they can be converted into each other (Godelitsas et al. 2003), therefore the presence and ratio of lead salts in a given pigment sample will depend on variables during the production process – such as the location of the ceramic container within the stack itself and the quality of the starting materials (Homburg and Vlieger 1996: 39) – or on processing methods. Some reports in the late 19th and early 20th century state that the freshly produced pigment contained some residual lead acetate (Carlyle 2006: 15).

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

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

Materials and methods

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

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

Reconstructions were executed with traditionally prepared stack-process lead white, thoroughly washed with distilled water. Vinegar for grinding with the lead white was prepared from organic, sulphite-free red wine and vinegar culture (bacteria). Lead white pigments, further
processed by grinding with vinegar and/or further water washing, were subsequently made into oil paint by hand grinding with poppy oil extracted from a single seed lot from a single supplier. The paints were spread on polyester film (Melinex) with a hogshair brush and with a drawdown bar. All dry pigments produced were analysed with X-ray diffraction (XRD), and the oil paints were then analysed in cross-section with SEM-EDX. Colour measurements were made on the paint films using a Konica-Minolta spectrophotometer.
### Table 1 Historical recipes for washing stack-process lead white.

<table>
<thead>
<tr>
<th>Author</th>
<th>Recipe Description</th>
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<tr>
<td>Pomaro, G. 1500–1600.</td>
<td>I ricetarti del fondo palatino della bibliotheca nazionale centrale di Firenze. Milan: Giunta Regionale Toscana Editrice Bibliografica, 98 (Pal. 796: c. 5v)</td>
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<tr>
<td>Andriessen 1552.</td>
<td>Viervoudig tractaebboek. Kampen: Steven Joessen, 55</td>
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<tr>
<td>Anon. 1668.</td>
<td>'Secrets in the noble arte of miniatura or the art of limning' . London: British Library, Ms. Additional 12461, 38–9</td>
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<tr>
<td>Veen, J. van c. 1650.</td>
<td>'De wetenschap ende manieren om alderhande couleuren van say van sayetten te verweren' . The Hague: Royal Library, Ms. 133K44, 119</td>
</tr>
<tr>
<td>King, D. 1653–57.</td>
<td>'Secrets in the noble arte of miniatura or the art of limning' . London: British Library, Ms. Additional 12461, 38–9</td>
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</table>

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 sottilissima con aqua.* Prima macinerai la biacca sottilissima con acqua; poi la lava 3 o 4 volte et lasciala secchare in su la pietra, et poi la tolle et serba in una carta.

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 humidiify 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.

*Lootwit wrytten op een harden steen met schoon water ende wilmont schoon hebben so als wel ghewevesen liggen op die harde wrrftseen en besprengent met schoon water ende latent soo liggen ende bleken in die heete son ende alsit drooghe is salimont weder vochtich maecchen op den sten ende wryjent een poes ende laatent wederom drogen ende bleken tot vier oft vijf reysen toe. Dat is tschoonste wit datmen kan gheweijden behouden dat ghie eerst wel uit geslesen hebt blauwe loot jumper in valt int wryven dat moetmen alzijt wel wae nemen ende uit doen oft dat Lootwit souder werckelijkk af smetten.*

Lead those Colours that are to be Grownd; I shall not run over every Colour particularly, but shew you how to grind one Colour, which take as an example for all the rest.

To grind it do thus; Take a quantitie thereof, or of any other Colour to be grownd, being cleansed from all manner of dirt or filth, which you only one is refined, the other not.

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, and let it be an example for all the rest.

Grind those Colours that are to be Grownd; I shall not run over every Colour particularly, but shew you how to grind one Colour, which take as an example for all the rest.

To prepare white excellent.

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

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

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

Daar toe dan kiezen uit de dikste Schulpen, als de beste, die men in zeer schoon en helder water vrijt op een goede keystone, die niet te hard of te glad wezen kan; en alzo is gerevven, zet menze 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, Lijznatu-oly en andre bekenden overtreff; waar na menze in een rein Schulpie of kommepte does, en er schoonwater op zet, om niet te verdroggen; en dus kainenze goed houden; om als t voordig is, gebruikt te […]. T Goede ongemaalen Lootwit bereiden op de zelwe wyze, als het Schulp-wits; dog t is gemakkelijker om vryven;

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

The instruments and Materials us’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 Linseed 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 wijven wil zo noemt eerst wat loot-wit om de stoen steen wat zayver te maken en als t gewreven is zo doeter wat indigo bij, want dit wit dan niet zuyver genoeg is om alleen te gebruiken, daer na noemt ander loot-wit en die zal zuyver zijn. T wit kint gij wijven met water; en laeten droogen en temperent met suet olijf of lijn olijf. Loot-wit vrijft met pis of asijn en als gedroogen is en gij die wilt gebruiken zo tempertse met olij.

390–94: Lead white is ground with clean water; if it is not beautiful so leave it spread on the stone after it has been ground and sprinkled with clean water and leave it thus to bleach in the hot sun and if it is dry it will again be humified 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.

Loodwit vrijten met schoon water; wilmens schoon hebben zo laet het wyt gespreygen leggen op de steen als t gewreven is en besprengen met schoon water en latent zoo staan bloeken in heete zon en als t droosch is zal ment weder roothich maken en wijven weder een wijf sijts en wennen en bloeken tot de 5 maal toe dit is schoon wit en als ment verwerken als ment verwerven en temeert voor een eind of 4 of 5 maal toe dit is schoon wit en als ment verwerken als ment verwerven en temeert voor een eind. Nota. Als men dit loothwit vrijft zo moet men het loot datter gemenneke in is daar wyt seken of het zonder zonderlinge af besmet worden.


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

Het loodt-wit magh oock wel van versten af aen met water gewreven worden dat vinden sommige beter, maer het venets wit moet van versten af in olie gewreven worden, om dat men het water daer niet uijt temperen kan.


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 broi ces écailles sur une pierre dure, comme porphyre, avec la molette & de l’eau claire, & le plus proprement qu’il est possible pour avoir un blanc pur; desfois ces écailles sont couvertes d’une matière grise ou jaune qu’il faut retasser avant que de les broyer, 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 broié à l’eau et ensuite on broie ces écailles avec la molette et de l’eau claire, et on le laisse bien secher, & on le peut garder tant qu’on veut.

Sprong, U. 1738. *Kabinet der verf-stoffen.* Amsterdam: Jacob Graal, 8

For Deadcolouring you may grind white lead in Lynseed Oyle.

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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 Loont Wit te maken.

Doet die te zamen in een steene vysel, en giet een wyng Water daaron, en stampt 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 papi, doet dan de verwe met een lepel in een of twee potten, en zet het in de zon, en laat het hard worden, dan is het gemaakt.

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

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

Schelpwit. Bereiding.
Hier van zyn volgens veele twee soorten, wier eene Venetisch, de andere Inlandsch genaamt word; dog ik hebbe nooit meer dan een soort gezien, ín 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.

Bays, E. 1774. Nieuwen en Volkomen Woordenboek (10 vols), vol. 6: K-L. Amsterdam: S.J. Baalde, 754
This lead white is ground in a porphyry stone with a little water, and made into a dough, which is made in moulds into small pointed breads, which are dried for transport;

Men wryft dit loodwit op den porphyr steen met een weinig water, en maakt er een deeg van, dat men in vormen tot kleine spitsvrye brooden 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, eenen langen tyd

White is made up 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.


148–9: Seventh section. About white paints. 1. White lead white. After the lead has been transformed into lead white through the vinegar vapors, it is ground on large grinding stones, which in large factories may be most economically driven by water force like machines, as tenderly as possible and humidified with water, so a thick pulp results. Then the lead white is cast in moulds, which are normally pyramid shaped, and dried in summer in the open air, in winter however in a moderately warm oven.

Siebenter Abschnitt. Von der weißern Farbe. 1 Weiße Bleiweiß.
Nachdem das Bléi durch die Dämpfe des Eifigs in Bleiweiß zernaget ist, so wird es auf großen Reibesteinen, die als Maschinen in einer großen Fabrik am vorteilhaftesten von Wasser getrieben werden können, auf das zarteste gerieben und dabei mit Wasser angefeuchtet, daß ein dicker Brei daraus wird. Sodann wird das Bleiweiß in Formen gebildet, die gemäßiglich pyramidenförmig sind, und im Sommer an der Luft, im Winter aber in einer mäßig warmen Stube getrocknet werden.

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

Die Fabrik reibt das Bleiweiß zwar auch unvermiscet; allein, grötlentsheils erhält es auf der Mühle einen Zusatz von Kreide. Das reine Schieferweiß schüttet man blos auf den obersten Mühlstein, benetzt es mit Wasser, und wiederholt dieses zum öftern, während daß es gemahlen wird. Es läuft durch gedachte Rinnen vom dem obersten Steine zu den drei übrigen, und wird von allen 4 Steinen vryft het sterk met schoon regenwater op een steen, een lange tyd.

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 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.


O economic cas Courant, 15 October 1800. No. 167, 82

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

The lead, chalded by the vinegar into lead white, is ground very fine on large grinding stones, which in a factory are mostly 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 leaves are dried in summer in the open air, and in winter in a moderately heated room.

Oeconomische kundigeden. Over het LOODWIT, het fabriceren van, en den Handel met hetzelfe. Het Lood, door den Azeyndamp tot Loodwit verkaald zynde, wordt op groote weijsstienen, die by eenze Fabriek het voordeeligst werktygklyk door het water gedreven worden, zeer fin gewreven of gemalen, en met water tot een dikke brei aangedemengd. Vervolgens vormt men het Loodwit in vormen, die doorgaans de gedaante hebben van een stompsuikerbroederen; wordende deze broodjes by den zomer in de open lucht, en ’s winters in een taamlyk warm vertrek gedroogd.

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

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

Om het wit, welke soort ook, ongenoemt schoon te hebben wijfje met hetzelze schoon in water, laat het drogen en dan fijn stoten en met blanke verse papaver of henolie wreven.

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 muller. During grinding you add some water, to make the mass drain off better.

On top of the container, into which the lead white drains from the mill, you place a hair sieve, through which the mass must pass into the container, to retain the coarse materials. When the container is full, you place another one underneath and continue grinding, until all is done. In the containers, in which the lead white runs off, it settles at the bottom, and the water standing on top is removed with taps or holes. Afterwards you pour the lead white on a linen cloth, roughly stretched on a frame, where the [remaining] water drains off. Then it is further dried, either on a tile stove, which one fuels with a small fire, and then applies the mass on top, where it quickly dries; or most commonly like this: one takes planks with holes, in which conically shaped earthenware pots are placed. The hole, which these pots have at the bottom, and through which the water runs out, is closed with paper; the pots are lined with bright blue paper, and then the mass is put in. When the moisture is removed, then the little lead white huts are placed on a wooden board in the air, to dry them completely. Now the lead white is ready for transport. The more the mass is washed with water, the whiter the lead white becomes, and with when adding the finest, whitest and cleanest chalk it also results in the most beautiful lead white. The remaining black deposit consists of undissolved lead, which may be reused for a fresh batch.

Diese Mühle [= mill for grinding lead white] kann man auch im Kleinen machen, und zwar so: Man läßt einen großen Stein, wie eine halbe Kugel, auf einen tiefe Hohl aushauen, oben am Rande wird eine kleine Rinne eingehauen, durch welche die Masse während des Reibens in ein anderes untergestelltes Gefäß abreichet. Dieses schöne Weiß wird mit zum Glasuren auf gemeines Bleiweiß gebraucht.

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

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.

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 onvergelekkelijke witte loodkler wordt gemaakt van lood-wit, dat uitgezocht en wel op een’ porphiersteen 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 afgegooten hebbende, roer het dan weder door met azijn; herhaal dit nog een of twee maalen, en gij zult een uitsluitend fraai wit, beide voor water- en olieverven geschikt, bekomen.


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

La biaccia di commercio per depurarlo, si usas prima polverizzarla, e poi sopra gettarvi piú d’una volta dell’acqua bollente; ed à molto necessaria fare questa operazione a quella di Kremnitz, perché contiene un’colli’ animale, donde ripete la sua tenacità.


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

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

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

***) Slaking is operated as usual. One has a large, square tray, which has 7 to 9 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 lor some time, then pressed into earthenware or sheet metal moulds, which have the shape of small conical hats, and left to dry first in these, then in the open air * (during which very sulphurous vapours must be kept away) and then wrapped in paper.

*) 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 raapt dann den Mist weg, nimmt die Töpfe heraus, schaubt das an dem Metall hängende Bleiweiß ab *, nachdem man es befeuchtet hat, um das Stauben zu verhindern, 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 dis nöthig ist, und läßt es malen †). Oft wird es zuletzt noch geschlämmt.


†) In Holland geschieht das malen auf drei nebeneinander stehenden und durch Eifere getriebenen Mühlen. Die erste malt grob, die zweiten 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.

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TO PREPARE WHITE EXCELLENT...
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 pealash being added to it, it is changed into white lead, of a beautiful whiteness, and is sold for choice purposes: the remains 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 thisceruse; 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 écaill s, que l’on met à part, pour les repandre dans le commerce sans autre préparation. Les spirales sont déroulées, on en retire des écaill es plus petites et plus friables, 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 con naît. |

| Vergnaud, A.D. 1831. Manuel du peintre en batiments, du fabricant de couleurs, etc. Paris: Roret, 12 |
| Silver white. This white is used by easel painters, and is nothing but a lead white of the first quality, which one prepares with more care, and which one releases, by a large number of washings, of every possible impurity. 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 3¾ 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 hölzernen, dicht verschlossenen Kasten zermahlen, [gesiebt], sodann unter verticalen oder horizontalen Granitsteinen mit wasser fein gemahlen, [der] Brei in conische, nicht glasierte Töpfe von 5 Zoll Höhe und 3¾ Zoll Durchmesser am oberen weiten Theile gethan, welche auf einem Trocknertrog stehen und täglich einige Male gerührt 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. |

| 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 ½-1 turn per second. The pulp is scooped into the little “Sarge” [meaning unclear, probably hole in the centre of the stone] of the running stone with a copper spoon with a long handle and so much is added, that the “Sarge” is filled. It takes some time, before its contents have sunken down, when it is again filled, until bit by bit a batch, for instance 10 Centner has gone through. A worker can operate 4 to 5 stones, standing besides each other. The material that collects in the “Sarge” of the lower stone is moved forward to the outlet with a shovel more often, where it falls into a smaller vessel. During first grinding it is often necessary to raise the upper stone a little, because the mass is very thick and therefore does not easily flow between and through both stones. When everything has been ground and the ground mass is a thick pulp, the stone is ground clean by rinsing it with water, the hole of the base stone is washed, for which a coarse brush or a scrubber is used, and then the same pulp is ground more finely several times in the same manner with more closely placed stones. It is better, however, and this is most often done, that the raw lead chalk is passed through one stone and that the fine grinding is done in some other set of stones, which are turned simultaneously, so what comes off the first stone is scooped onto the second, from there onto the third and fourth stone and the grinding takes place evenly and uninterrupted. If soft lead white is made, then one can act the same way both with pure lead white and with mixed types until the finishing; but to prevent it from becoming hard, careful washing is inevitable. For rinsing one needs a number of large vessels, the larger, the better. These vessels are filled with water, the ground lead white is added in and shaken very well, which is very difficult, because it does not dissolve easily. Then it is left to settle, until the liquid is clear and can be drained off. This stirring with fresh water, settling and draining is repeated several times. Then the very thick lead white pulp is placed in a filter, then in presses, to remove the water and is then in irregular chunks left to dry in air or in drying 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 acetate, and is too dilute to be further usable. This loss can amount to some percents. To prevent this, one can do two things. One adds to the first water, with which a lead white is stirred, one ‘Maß’ of a crystal soda solution, which results in a precipitation, in which the dissolved lead settles as carbonylic 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 carboyllic 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 elevates it when it is somewhat useable, however not very pure lead white has accumulated inside, and then feeds it again.

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 finished in another, or the same, stove room. […]

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 ground stuff is shovelled into the hopper of a cylindrical sieve, but carry it in scoops or ladles.

IV. The white lead is mixed with water in troughs, so as to form a paste which passes successively through several horizontal mill-stones before it is thoroughly comminuted. This wet grinding is absolutely without danger, since the men do not touch the white lead with their hands, but carry it in scoops or ladles. For preparation of a white lead for washing, it is the usual set-up of the German mills. During rinsing in large factories a substantial amount of lead is lost yearly, which is washed out and drains off with the washing water and lead acetate, and is too dilute to be further usable. This loss can amount to some percents. To prevent this, one can do two things. One adds to the first water, with which a lead white is stirred, one ‘Maß’ of a crystal soda solution, which results in a precipitation, in which the dissolved lead settles as carbonylic 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 carboyllic 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 elevates it when it is somewhat useable, however not very pure lead white has accumulated inside, and then feeds it again.

Das Vernahlen kann man, wie schon gesagt, auf zweierlei Weise vor sich gehen, je nachdem hartes oder weiches Bleiweiß dargestellt werden soll. Wird hartes dargestellt, so kommt der Teig des Bleikalks oder das mit Wasser angerührte trockene Pulver des Bleiweißes auf die Mühle, während sich die Steine gewöhnlich so bewegen, daß sie in der Secunde 1½ - 1 Umdrehungen machen. Man schießt den Brei mit Hilfe eines langgestielten kupfernen Löffels in die kleine Sarge des Läufers und gibt so viel auf, bis die Sarge voll ist. Es dauert dann einige Zeit, bis deren Inhalt niedergesunken ist, worauf man wieder nachfüllt, bis nach und nach eine Partie, z. B. 10 Centner durchgegangen sind. Ein Arbeiter kann 4 bis 5 Steine, die nebeneinander stehen, bedienen. Was in der der Sarge des Bodensteines sich von Gemahltem ansammelt, wird durch ein Schlaufeichen öfters nach vorn in den Ablauf geschafft, wo es in einem kleineren Ständer fällt. Bei dem ersten Mahlen ist es häufig nötig, den Stein etwas höher zu stellen, dagegen die Masse sehr dick wird, läßt sie sich geruhen unter und durch die beiden Steine. Wenn Alles durchgemahlen ist und was das Gemahlene einen zären Brei darstellt, so wird der Stein durch Nachspülen von Wasser rein gemahlen, die Bodensteincharge auch ausgewaschen, wozu man sich eines groben Haarpinsels oder einer Bürste bedient, und nun wird derselbe Brei noch einige Male auf eine ebene dieselbe Weise bei enger gesteilter Steine hintereinander und gemahlen. Besser ist es jedoch, und so wird es auch meistens gehalten, daß man den rohnen Bleikalk stets einen Stein passieren läßt und das Feinmahlen auf einigen anderen Gängen, die zu gleicher Zeit in Bewegung sind, ausgeführt wird, dann wird dann dasjenige, was vom ersten Steine kommt, auf den zweiten, von da auf die dritten und vierten Stein geschafft und das Mahlen geht dann regelmäßig und ununterbrochen fort.


Das Vernahlen zu weichem Bleiweiß kann aber auch von vorn herein auf eine Weise erfolgen, wodurch das Auswaschen und Zertheilen leichter vor sich geht. Der Bleikalk wird nämlich mit viel Wasser vermasselt, 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 Bodensteincharge herausläßt. In diesem Fall ist leicht eine solche Anordnung der Mahlgänge möglich, da man sie durch das stehende Triebrad herum stufen- oder treppenweise aufgestellt wird, 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 Abwässerungsgestonde, worin das Bleiweiß, wie vorhin schon erwähnt, abgewaschen wird. Dies ist die gewöhnliche Aufstellung der deutschen Mühlen.

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

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

The salt mentioned by King most probably consisted of lead acetate. During water washing of lead white carried out by the HART project, lead acetate levels were monitored; after numerous water changes lead acetate was no longer detectable. An overview of water-washing recipes within the period under investigation (Table 1) shows that the main methods used were either washing with large amounts of clean water, repeated grinding with water on the slab, or a combination of both treatments. Comparison of XRD analyses of unwashed and water-washed lead white confirmed the findings of the
Historical recipes for processing lead white with vinegar.

### Table 2

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To render *bianca* extraordinarily more white. Take lead white in flakes, choose the most beautiful, and grind well on the marble with vinegar, and it will become black; then take an earthenware beaker full of water, and wash your white well, then let it settle well at the bottom, and pour off the water by inclination. After grinding with vinegar and wash; and having done this approximately 3 or 4 times, you will have a *bianca* that will be perfectly beautiful for miniature painting, as well as oil painting.

Per rendere la *bianca* più bianca straordinariamente. Prendete *bianca* di piombo in scaglie, eleggete la più bella, e macinate la bene sul marmo con aceto, e diventar nera, allora prendete un vaso di terra piena d’acqua, e lavate il vostro bianco bene, poi lasciatelo bene dur in fondo, e verrate l’acqua per inclinazione. Tornatela a macinare con aceto et a lavare; e fatta questa operazione med. 3 o 4 volte, che havera una *bianca* che sarà perfettamente bella tanto per miniare, quanto per dipingere a olio.

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**TO PREPARE WHITE EXCELLENT...**

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...But if you use white lead, first rectify it with white wine vinegar, this will cause a fermentation, and the white will soon settle; then pour off the water, and wash it with common water. The method of washing it is thus: Put the powder into a glass of water, stir it about, and presently pour off the water, while it is white, into some other clean glass or vessel let it settle, and then pour off the water from it, and it will be excellently fine. Some say it is better, if some rectified spirits of wine be pour’d on it, which will clear it from any dross that may be in it; this (as it is very probable) must be pour’d off, when the spirit of wine has done its work.

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...Le spirit d'apricot, ou de citron, ou de vin blanc, ou de spirit es purifiés; et l'ajouter à cette eau, qui lavera la peinture. De cette maniere, on obtiendra un excellent blanc, pure et nettoyé des traces de plomb qui l'ont tache de noir, et qui en est la cause.

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...As you pour the spirit off, you will see that the white is not subject to darkening because of the badly dissolved lead particles that it contains, or at least very disposed to altering itself by the least contact with the air; the vinegar achieves the complete dissolution of these particles, much better than a mineral acid, because it does not contain phlogistique; at least also developed: it is good for this reason only to purify the amount that you need.

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...Puis verrez que ce blanc n'est sujette à noircir qu'à cause des particules de plomb mal dissoutes qu'il contient, ou du moins très-disposées à se reviviser par le moindre contact de l'air; le vinaigre acheve l'entiere dissolution de ces particules, beaucoup mieux que ne seroit un acide minéral, parce qu'il ne contient pas de phlogistique, du moins aussi développé: il est bon pour cette raison de non purifier qu'measure qu'on en a besoin.

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...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.

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...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.
Recipes generally specified thorough water washing after grinding or washing lead white with vinegar before use. 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 would discolour 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.

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

<table>
<thead>
<tr>
<th>Author</th>
<th>Description</th>
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<tbody>
<tr>
<td>Mayer, T.T. de 1620-44. Pictoria Sculptoria &amp; quae subalternarum artium. London: British Library, Ms. Sloane 5052, 96v (Paulus van Somer) Lead white ground first with water, then washed &amp; allowed to settle, decanting the turbid water, makes a deposit that is very beautiful, &amp; dies less than the deposit.</td>
<td></td>
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<tr>
<td>King, D. 1635-57. Secrets in the noble arte of miniatura or the art of limning. London: British Library, Ms. Additional 12461, 39-40</td>
<td>Mr. Hillards manner of preparing Ceruse. 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 setled in the bottome dry by evaporating. Then in tempering it with gumme use it at your pleasure.</td>
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To prepare white excellent...
Table 3 Historical descriptions for pigment decanting or other methods of particle size measurement cont’d.

While the lead white formed in this operation [= 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 emplisies 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 obtenu dans cette opération [= blanc de Krems] n’a pu acquérir la dureté de celui qu’on obtient par la méthode hollandaise [= stack process], il n’est pas nécessaire de broyer; on l’obtient très divisé par 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 éclats de blanc de plomb, séparées préalablement du métal qui n’a point été attaqué. On y fait arriver de l’eau d’un réservoir supérieur, et l’on renvoie fortement avec un rable: l’eau déborde bientôt, s’écoule dans la seconde case, puis dans la troisième, et arrive ainsi successivement dans la neuvième.

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

Note: The table and text provide historical descriptions and experimental observations related to the study of lead white pigments, focusing on the effects of washing and grinding with vinegar on the composition and particle size distribution of the mixed pigments. The text includes references to historical sources and experimental methods used to study the lead white pigments from different periods and regions, highlighting the importance of washing and grinding techniques in the conservation and analysis of these materials.
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. Research by de Behault (2010) showed that small-sized lead white particles may have been selected by artists wishing to optimise blue-hued scattering effects, as seen for instance in the cool grey skin on blue grapes.

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

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.

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 (Brouvland of Everlo, Belgium, purchased 18/9/2010) was added to 500 ml sulphite-free organic red wine (Stellar Organics, Shiraz, South Africa, imported from Coenecoop Wine Traders B.V., 2742 RC Waddinxveen). The liquid was allowed to acidify during four weeks in a cool, dark place. The resulting vinegar had a slightly pink colour and a pH of 3–4 (Macherey-Nagel pH-Fix 0–14).
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 microdiftactometer with a general area detection diffraction system (GADDS) two dimensional detector (Bruker AXS, Karlsruhe, Germany). Powdered samples were applied in a little...
cedar oil on a Silicon zero diffraction plate. Diffractograms were acquired in reflection mode with CuKα radiation (40 kV, 30 mA). The GADDS software was used for integration and the Bruker AXS Eva software for phase identification using the PDF database.

9. JEOL 5910LV with thermo scientific energy-dispersive X-ray spectrometry system with Noran System Six software.
10. Konica Minolta CM-2600d spectrophotometer, white calibration 7004450.
12. The settling speed of particles depends not only on their mass and density, but also on their shape.
13. Earlier experiments, repeated during the present research, ruled out the possibility that very fine grades of lead white could be produced by extensive grinding on the slab (Carlyle 2006).
14. Procedure according to ASTM 2001 standard to determine the Yellowness Index (YI) E313–73: illuminant D65 (daylight, colour temperature 65°), 10° observer (CIE 1964), three automatically averaged measurements in three different locations. Vinegar-treated lead whites had a ΔYI roughly twice as large as the water-treated lead whites.
15. Mulder 1865: 302–3; Carlyle 2001: 260. Experiments undertaken by Rhodes and Van Wirt (1923) showed that slightly basic lead carbonate retarded the initial oxidation of linseed oil and did not promote final oxidation as much as a more basic lead white.

References


TO PREPARE WHITE EXCELLENT...


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