Historical recipes for preparatory layers for oil paintings in manuals, manuscripts and handbooks in North West Europe, 1550-1900: analysis and reconstructions

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Chapter 12 Flour paste in recipes for preparatory layers for oil painting, 1550-1900

After the linen has been stretched and nailed onto a frame or board of the intended size, brush it very well with bookbinder starch (which preparation I will explain at the end of this paragraph), with the aid of a small plank of about 4 finger widths long and 3 fingers wide, sharp at the bottom and somewhat thick at the top.

Cröker 1729

12.1 Introduction

Flour paste or starch paste have rarely been identified in preparatory layers of oil paintings and, in particular, their use in pre-nineteenth century paintings has been reported infrequently (Appendix 19, Table 12.1). While these published examples represent exceptional findings in actual artworks, there are a significant number of historical recipes mentioning both flour and starch as binders for size and ground layers for canvases (Appendix 19, Tables 12.2a & b). In some North European recipes from the sixteenth to the nineteenth century, flour or starch is advised instead of a glue size layer. It appears less frequently as a binder for ground layers in recipes prior to the nineteenth century, and when mentioned it is described only in Italian and German recipes.

What causes the discrepancy between the regular occurrence of flour and starch in historical recipes and their infrequent identification? Firstly, it is possible that the recipes mentioned in these sources do not correlate with actual painting practice. However, a discrepancy could equally be caused by the fact that starch is not very obvious as a size layer or in the ground matrix. The recipes listed in Table 12.2 demonstrate that flour or starch is heated during preparation. Heating to a temperature that thickens the paste, destroys the characteristic starch granules. Without these granules, no sign for the presence of starch is seen when the layer is investigated in cross section with visible light and ultraviolet radiation. A factor that further complicates starch identification is the fact that in some recipes the flour or starch is mixed with glue and/or oil. ‘Standard’ chromatography protocols for the identification of oil painting grounds do not always include a search for starch, in particular if other binders are located in the layer. It is only recently that analytical methods have been developed that allow for the identification of starch in complex mixtures also containing animal glues and oils.

1 Cröker 1729: 74-5
2 This chapter has not yet been submitted for publication. A short version of its contents has been presented in a poster (Stols-Witlox 2013, publication due in 2014 from Archetype London) and a longer publication is in preparation.
3 Flour is defined here as the material obtained by milling cereals, starch is a carbohydrate product extracted from flour according to procedures described below
4 See also Chapters 5 and 6
5 This was noted earlier in Carlyle et al. 2008b: 126

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In order to determine if recipes relate to actual painting practice, the chemical properties and visual characteristics of starch or flour bound layers need to be further examined and identified. This chapter explores the history and sources of cereal grains employed for flour and starch pastes, and reports on how reconstructions of flour paste and starch paste preparatory layer recipes, that are executed to investigate the working properties and visual characteristics of such layers, can be used to these ends. More knowledge about the characteristics of flour paste layers will result in improved criteria for their identification.

12.2 Methodology

As a first step, an analysis of historical recipes for flour paste and starch paste grounds and size layers was carried out in order to identify variables regarding boiling time and paste composition that are relevant for investigation by reconstruction.

It is vitally important to employ materials with a close resemblance to historical ingredients in order to recreate valid products destined to provide information that can be compared to actual paintings. This extends both to the flour types employed, as to the milling methods and to the starch production methods. The reconstructions presented here were made with historical flour types (varieties, composition, flour particle characteristics) obtained using historical preparation methods. Reconstructions contained pigments and linseed oil that are produced according to historical methods.

Reconstructions were kept in a climatised laboratory space for natural ageing. Artificial ageing was executed for 2479 hours at an elevated temperature 35°C and a relative humidity of 60% on a second set of samples. Samples of naturally and artificially aged samples were embedded as cross sections in polyester resin (Polypol PS 230) and studied and photographed with visible light and under UV. Staining with a potassium iodine/iodine stain was also performed on the cross sections. A drop of the stain was applied to the cross section, allowed to react for thirty seconds and the excess was removed by soaking with a paper tissue. Polarised light microscopy was performed on the starch powders to characterise all starches.

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6 While Carlyle et al. 2008b carried out historically appropriate nineteenth century flour paste ground recipes, the use of starch alone was not explored, nor the use of flour and starch paste in earlier recipes.  
7 Artificial ageing was executed at the RCE (Dutch Cultural Heritage Agency) in a Vöth Industrietechnik VC0020 climate chamber. An elevated temperature was chosen to speed up degradation processes. An even higher temperature was considered risky as it could liquefy the animal glue. The relative humidity was slightly raised, as moisture is described as one of the factors influencing flour paste degradation in historical sources.  
8 Samples were examined on a Leica DM 2500M microscope with a 100 Watt HbO UV lamp, UV filterblock A/DAPI-HOECHST "UV". Excitation: BP 360/40, dichromatic mirror: RKP 400, Emission: LP 425. Photographs were taken with Leica EC3 camera.  
9 Embedded in Polypol PS 230 polyester resin.  
10 The stain solution chemically binds to the amylose present, which results in a dark blue (black almost) staining of the starch-containing area. The stained starch containing material can be easily identified using (visible/UV) light microscopy. See Table 12.6 in Appendix 19 for PLM photographs. No differences were found between the starches.
11 Stained with potassium iodine-iodine solution prepared 14-4-2008. See Schramm and Hering 1995: 205 for a recipe for a KI-I stain: 1.7 gr potassium iodine and 2.5 gr iodine dissolved in 100 ml water.

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12.3 Textual analysis of historical recipes that include flour or starch in preparatory layers

12.3.1 Ingredients

As early as c. 1400, Cennini provides a recipe where starch is added to warm animal glue for a size layer, and the same mixture is used, with the addition of ‘gesso sottile’, as a ground layer on canvas.\(^\text{12}\) Table 12.2a in Appendix 19 demonstrates that generally, flour paste is advised as a size layer only for canvas, not for panel.\(^\text{13}\) For instance, Eikelenberg in his manuscript (1679-1704) advises using a glue size layer for panel, but a flour paste for canvas sizing.\(^\text{14}\) Paste preparation recipes specify heating flour or starch either in water or in animal glue. Recipes for flour or starch paste bound ground layers (Table 12.2b) advise the following pigments or fillers: lead white, pipe clay, gypsum, pumice powder or bone ashes. Flour- or starch-based layers are usually covered with subsequent oil-based ground layers.

Several additions are mentioned to modify the paste properties, honey being described most frequently, in particular in Spanish recipes but also by the nineteenth century German author Dietrich (1871).\(^\text{15}\) Honey is very hygroscopic and by binding water, it acts as a paste plasticizer.\(^\text{16}\) Montabert (1829) mentions additions of garlic for greater strength, of vinegar, laurel and nut tree leaves to deter insects and of resin to strengthen the paste.\(^\text{17}\) Some recipes furthermore specify the addition of an oil or of turpentine (See Table 12.2a). Reifsnyder (2013) in the context of paste-based lining adhesives writes that Venice turpentine makes pastes more sticky and flexible, and that it may play a role in making the paste more resistant to humidity from the environment.\(^\text{18}\) Testing of reconstructions with and without Venice turpentine executed by Carlyle led to the conclusion that the turpentine stiffens the layer.\(^\text{19}\)

12.3.2 Historical paste preparation methods

Unfortunately, not many authors of historical recipes provide details for the preparation of the flour paste itself. Casual descriptions demonstrate that its preparation is considered common knowledge. Eikelenberg (1679-1704) simply talks about a ‘paste of wheat flour’,\(^\text{20}\) the Wiltshut manuscript (1726-9) describes the use of a ‘porridge of flour, when boiled, a little linseed oil added’,\(^\text{21}\) Ibbetson (1803) talks of ‘a very thin starch’\(^\text{22}\) and Sully (1809-71) advises ‘paste in which was a little Venice turpentine’.\(^\text{23}\)

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\(^{12}\) Cennini c. 1400, Frezzato 2003: 182-3  
\(^{13}\) See Chapters 5 and 6  
\(^{14}\) Eikelenberg 1679-1704: 403-5  
\(^{15}\) Pacheco 1649: 68; Hidalgo 1693: 137; Palomino 1715, 1724, vol. 2 1724: 149; Dietrich 1871: 21-2  
\(^{16}\) Reifsnyder 2012: 419  
\(^{17}\) Montabert 1829: 176  
\(^{18}\) Reifsnyder 2012: 419  
\(^{19}\) Carlyle et al. 2008b: 128  
\(^{20}\) Eikelenberg 1679-1704: 385  
\(^{21}\) Wiltshut manuscript 1726-9: 78  
\(^{22}\) Ibbetson 1803: 11  
\(^{23}\) Sully 1809-71: 156
Fortunately, a small number of authors do include preparation instructions: Cröker (1729) describes how a little boiled water is added to flour, stirred to remove lumps, after which more water and flour are added. The consistency is correct when, while still warm, the paste forms little ‘towers’. De Montabert (1829) explains that flour and water should first be mixed, then heated on a fire until thickened.

A very detailed description of the preparation of flour paste is provided by Hundertpfund (1847): Flour is slowly stirred into water. The mixture, thin as milk, it is heated until it thickens. More water is then added and the mixture is allowed to boil slowly for half an hour, after which it is mixed with pipe clay, which has been soaked before in water and stirred to form a milky liquid. Hundertpfund explains that ‘by continual slow boiling, it becomes smoother and smoother, so that it may afterwards be thinned with water, according to liking’. The resulting liquid is sieved through a hair sieve and applied to the canvas with a brush in three to four coats.

In contrast to Hundertpfund’s recipe, which specifies prolonged heating on the fire to make the mixture smoother, both Sully (1873) and Vibert (1892) advise removing the pan from the heat when it thickens.

12.4 Flour and starch: varieties, production methods and trade

12.4.1 Historical descriptions of the type of flour employed

In historical recipes, the flour type and quality are usually not specified. Table 12.2 in Appendix 19 shows that in most instances, the recipes just call for ‘flour’, sometimes adding a comment about the quality of the flour: ‘well-sifted’ (Cennini 1400, Palomino 1724), ‘fiore di farina’ (‘finest of the flour’, Borghini 1584), ‘flour or mill dust’ (Pacheco 1649), ‘rocken- oder staub-mehl’ (‘rock- or dust flour’, Cröker 1729) or ‘belle farine’ (‘beautiful flour’, Bouvier 1827). Wheat flour is specified in four recipes and two German recipes advise rye flour.

What kind of flour was used when no indication of the cereal source is provided? It is assumed that authors referred to the crushed wheat grains used for baking breads and pie crusts. This is a safe assumption since no other use of ‘flour’ is as common as the ingredient used for baking and because bread was the product baked in the largest quantities in the Western world, at least since Medieval times.

Whereas nowadays, wheat is the most common cereal used in bread baking in the Western world, in former centuries rye played a larger role. Other cereals grown were

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24 Cröker 1729: 77
25 De Montabert 1829: 176
26 Hundertpfund 1847: 108-9, 130; quoted by Knowlton 1879: 30-1. If this ground is too absorbent, Hundertpfund advises mixing the oil paint applied on top with wax or using a mixture of 2 parts dammar or mastic varnish and 1 part fat oil to which 1/20 part wax is dissolved.
27 Sully 1873: 024-5
28 Vibert 1892: 190
29 Pictorius 1747: 355; Müller 1750-1800 (transcribed in Lehmann 2002: 65); Grandi 1806; Montabert 1829
30 Hampel 1846: 22-5; Dietrich 1871: 21-2

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barley, buckwheat, oats and millet, but according to Karg (2009) they were not used for bread making.\textsuperscript{31} The division between rye and wheat is in part dictated by the soil type, rye being adapted to poor and acidic soils, whereas wheat requires relatively fertile soils.\textsuperscript{32} Rye and wheat were sometimes sown intermixed in a mixture called ‘maslin’ or ‘masteluin’.\textsuperscript{33} Belderok et al. (2000) write that until well after the Middle ages, poor people in North West Europe normally ate rye bread while wealthier people employed maslin.\textsuperscript{34} The fact that no further milling was required to produce rye bread from crushed grains means that production costs were much lower.\textsuperscript{35} Around the middle of the eighteenth century, wheat bread became more popular, but Belderok writes that in times of scarcity, a large part of the population would revert to rye bread. It was only when the industrial revolution led to faster and cheaper milling and flour processing methods, and when simultaneously the wheat price was lowered due to the import of cheap wheat from across the world, that wheat flour became affordable for the majority of the population.\textsuperscript{36}

In Europe, international trade in cereals, in particular wheat and rye, has a long history, starting in the thirteenth century with the Hanseatic cities as important wheat exporting centers.\textsuperscript{37} From the end of the Middle Ages on, Amsterdam became a main trading center for wheat, a position it retained at least until the end of the eighteenth century. Wheat first entered Amsterdam mainly from France and the Southern Netherlands, but during the sixteenth century, more and more came from the Baltic countries.\textsuperscript{38} Amsterdam exported inland by river and across the sea to Spain, Portugal, France and England. Also, Delft and Dordrecht functioned as trading centers, trading mainly in wheat that came from France and the Southern Netherlands.\textsuperscript{39} While Russia and the Baltic countries also became important producers of wheat, after about 1860 they lose their position as the largest export countries for wheat to the United States and Canada, who transported wheat across the Atlantic Ocean by steam boat.\textsuperscript{40} Belderok’s survey of wheat breeding in the twentieth century shows that around 1900, most North West European countries either imported or exported wheat.\textsuperscript{41}

\textbf{12.4.2 Characteristics of historical wheat}

Before the end of the nineteenth century, wheat was grown as ‘landraces’, which refers to local wheat varieties. Differences between such landraces are the result of selection by farmers of the most successful plants for sowing and consist of spontaneous mutations,

\begin{itemize}
\item Barley was used for brewing, oats and millet for porridges (Karg 2008: 97). Buckwheat was introduced in the Netherlands at the end of the Middle Ages, however already during the sixteenth and seventeenth century it was slowly replaced by other cereals. Bieleman 2008: 118.
\item Belderok et al. 2000: 3
\item Bieleman 2008: 203
\item Rye was hardly known in Mediterranean countries. Belderok et al. 2000: 8.
\item Bieleman 2008: 108
\item Belderok et al. 2000: 8. In some countries, especially in Scandinavia, but also in Germany, rye bread remained relatively popular next to wheat until the present day.
\item Belderok et al. 2000: 8-9
\item Belderok et al. 2000: 8
\item Van Tielhof 1995: 232
\item Bieleman 2008: 277-9
\item Depending on their location, they imported from Russia (for instance Finland); from North America, Russia and India (the Netherlands and Belgium); from France, German, Sweden or the Netherlands (Belgium); and India and Russia, North America, Australia and Argentina (United Kingdom) (Belderok et al. 2000).
\end{itemize}
natural selection or hybridisation.\textsuperscript{42} They are adapted to local circumstances and show a relatively large genetic variety.\textsuperscript{43} Zeven (1990) discusses the international ties between landraces. She orders the landraces grown in the Netherlands into the following groups: the Zeeuwse landrace group, the Gelderse (and Ruige Kleefse) landrace groups, the Ruwkaf Essex landrace group and the squarehead landrace group. The Zeeuwse landrace group covers French and Belgian Flanders, the Dutch province of Zeeland, part of Essex in Great Britain and probably adjacent regions. The Gelderse group was introduced into the Netherlands in the nineteenth century from West Germany. Also the Ruwkaf Essex group was introduced from the United Kingdom during the nineteenth century, but it was grown in the Netherlands only for a short time period. The squarehead group finally, was discovered in Great Britain in 1865 and introduced in the Netherlands in 1870. It was cultivated here from 1870 to 1900.\textsuperscript{44} Belderok describes how historical landraces grown in France are sometimes based on varieties introduced from England\textsuperscript{45} and that English and French types enter the German wheat fields.\textsuperscript{46} In Paragraph 12.4.3 it will be discussed that the exact composition of the flour will have varied depending both on the landrace and the growing conditions.

During the second half of the nineteenth century, the theory of evolution developed by Lamarck and by Darwin results in deliberate wheat breeding that aims to improve wheat quality, resistance to pests and wheat yield. Around 1910, combination breeding is introduced, which crosses indigenous and foreign varieties. The first half of the twentieth century sees the establishment of different breeding institutes throughout Europe.\textsuperscript{47}

\subsection*{12.4.3 Grain characteristics of wheat and rye}

In order to be able to identify wheat or rye in paint layers, their composition must be understood. A wheat grain or kernel consists of a coat (the ‘bran’), which surrounds a starchy endosperm, and the germ. Unfortunately, no specific information on historical wheat and rye varieties has been found to date in the literature.\textsuperscript{48} Information on the composition of modern wheat varieties indicates that the bran has a large proportion of dietary fibers (ca. 53%), and contains some proteins (ca. 16%), carbohydrates (16%), fats (5%), minerals (7.2%) and other components (2.8%). The mealy endosperm consists of carbohydrates (ca. 85%), proteins (ca. 13%), fats (ca. 1.5%), dietary fibers (ca. 1.5%), minerals (ca. 0.5%) and other components. The germ, from which the plant grows, consists of ca. 40% carbohydrates, proteins (ca. 22%), dietary fibers (ca. 25%), fats (ca. 7%), minerals (ca. 4.5%) and other components (ca. 1.5%).\textsuperscript{49} Precise percentages differ somewhat based on the type of wheat, so-called ‘hard’ wheats, with harder grains that have a more glass-like appearance, generally having a higher protein content.\textsuperscript{50} Wheat composition is influenced by other factors as well: protein

\begin{thebibliography}{9}
\bibitem{belderok2000} Belderok et al. 2000: 9
\bibitem{bieleman2008} Bieleman 2008: 131
\bibitem{zeven1990} Zeven 1990: 5
\bibitem{belderok20002} Belderok et al. 2000: 227
\bibitem{belderok20003} Belderok et al. 2000: 149
\bibitem{belderok20004} Belderok et al. 2000
\bibitem{carlyle2008b} Carlyle et al. 2008b: 124 write that they employed a historical wheat type with a 13% protein for their reconstruction, while modern wheats typically have a protein content between 7-10%.
\bibitem{percentages} percentages on a dry matter basis. From Belderok et al. 2000: 15-17.
\bibitem{belderok20005} Belderok et al. 2000: 18-19
\end{thebibliography}
content depends on growing conditions. Weather fluctuations and soil composition play a role, as does the time of year in which the grains are sown. Nordic winter wheat (sown in the autumn) seldom has a higher protein content than 12-13% of the dry matter, whereas spring sown wheat has a higher protein content (13-15% of the dry matter).

Nowotna (2006) writes that in comparison to wheat, rye grains have a lower protein content, a higher enzymatic activity and a higher amount of dietary fiber. Reifsnyder (2013) describes the protein structure of rye, which contains glutelin, while wheat flour contains glutenin. Rye also contains more pentosan gum, a non-starch polysaccharide which is very hydrophilic. Reifsnyder remarks upon the different quality of pastes with glutelin and glutenin, glutenin forming stronger chemical bonds.

Reifsnyder discusses the influence of protein composition and ratio on the elasticity of flour pastes for lining. The higher the gluten content, the more elastic the resulting paste. She explains that during heating, the ‘gliaden and glutenin forming gluten strands’ are cross-linked. The more the paste is stirred, the better the ‘full gluten structure’ is formed and the stronger the paste. Glutelin molecules form weaker bonds than glutenin molecules.

12.4.4 Cereal milling and sieving

In post-Medieval West Europe, wheat and rye were traditionally ground to produce powder on stone mills. Depending on the desired fineness, milling was executed in one or more runs. Roller mills, first used in Europe and in North America during the 1870-1890s, can strip the bran off the wheat or rye kernel, which results in a whiter flour. Modern flour production also removes the germ, which significantly improves shelf life but reduces vitamin content, and bleaching as well as additives are described in the literature.

To separate wheat flour from bran in traditional milling, bolting or sieving was the most common method. Historical descriptions of bolting cloths mention the use of finely woven woolen bags; later sources suggest steel sieves. The flour, placed inside the bolting cloth, was shaken. Bran and coarse flour stayed inside the bag, while fine flour escaped through the weave interstices. To prevent blockage of the sieves by the fine flour powder, rotating round cases with sieves were invented, with a system of brushes on the inside to prevent blocking of the interstices. These machines are called ‘bolting mills’. No information was found on the exact mesh used in historical sieves or bolts. Descriptions of old bolting

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51 Belderok et al. 2000: 91. A study of variability in French cereals shows a variation in starch content and composition depending on different years and regions, Metayer et al. 1993. BeMiller and Whistler cite studies that discuss the influence of growing conditions on the amylose content of several cereal types. In general the influence seems to be smaller than that of the cultivar and of cultivar maturity. BeMiller and Whistler 2009: 32.
52 Nowotna et al. 2006: 87-8
53 Reifsnyder 2012: 419
55 Campbell et al. 2011
56 Carlyle et al. 2008b: 124 describe oxidizing and reducing agents.
58 Modern mills use meshes in the range of 112 µ for very fine flour to 125 µ for course flour. Oral information Commandeursmolen Mechelen, date: 15-12-2011
methods lead to the assumption that meshes will have varied. Bolting lightens the colour to a ‘white’ flour, although stone milled flour is never as white as modern flours.

By sieving, whole meal flour was separated into several grades, which in earlier centuries probably followed local customs. The French 1782 *Encyclopédie Méthodique* describes the following grades: ‘fleur de farine’ (fine flour), ‘grosse farine’ (course flour), ‘les griots’ (‘semolina flour’), ‘les recoupettes’, ‘les recoupes’ (two lesser qualities containing more bran, probably similar to the English ‘grit and ‘grout’) and ‘le son’ (pure bran). Horses were fed the coarsest material, cows the ‘recoupes’, bread was produced from course and fine flour, and starch from the ‘semolina’ and the ‘recoupettes’.59

**12.5 Historical starch production**

12.5.1 *Historical production methods for wheat and rye starch: from flour or from grains.*

Historical descriptions demonstrate that the raw material used for starch production was not always the low quality flour and bran mixtures described in the eighteenth century *Encyclopédie méthodique* cited above. Comparative analysis of the recipes shows that different flour grades were considered suitable for starch production. Whereas some authors advise to use low quality flour with a relatively large amount of bran, others draw attention to the good starch quality that will be obtained when using very pure flour (See Table 12.3 in Appendix 19).

Some recipes prescribe flour as the starch source. Such recipes are provided amongst others by Estienne in 1653 and by the *Encyclopédie méthodique*.60 Estienne advises to mix the flour with water, remove the bran which floats on top, sieve the remaining flour through linen or a sieve, wash and sieve again and collect the ‘white flour’ that deposits at the bottom of the vat.61

In addition to flour and bran, starch can be extracted straight from the wheat grains. A description of a procedure to extract starch from wheat grains appears as early as 184 B.C. in Cato.62 Several historical recipes describe how to extract starch from wheat grains (see Table 12.3). The simplest procedure described in post-Medieval recipes consists of soaking the wheat grains in water until fully swollen, regularly replacing the water to prevent fermentation. The grains are then crushed, starch is ‘washed out’ and allowed to settle at the bottom of a tank or jar after the bran has been removed by sieving through a cloth. The starch is then washed and dried.63 Buc’hoz (1786) describes how the soaked wheat is placed in a strong canvas bag, which is pressed and pounded to squeeze out all the starch.64 Descriptions of this type of starch extraction continue until well into the nineteenth century (See Table 12.3).

59 *Encyclopédie Méthodique* 1782, vol 1: 16
60 *Encyclopédie Méthodique* 1782, vol 1: 16-18
61 Estienne 1653, vol 4: 526-7
62 BeMiller, Whistler 2009 : 2
63 *Kentucky Housewife* n.d.: 439
64 Buc’hoz 1786: 275

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Wagner (1860) includes a description of a new starch extraction method from flour, a process he explains as having been introduced in 1834 by E. Martin. For this procedure, a dough is made of wheat flour and water. After the dough has rested for 1/2 - 2 hours, starch is extracted by pouring water over the dough placed in a fine sieve and kneaded by hand or by machine. After slight fermentation, the starch is washed and dried.65

12.5.2 The role of fermentation

In contrast to those recipes that regularly replace the water used to soak the grains to prevent fermentation, other authors describe fermentation as a necessary step. In the entry on starch in his Encyclopedia, Nicholson (1808) explains the role of fermentation: ‘The farina [= flour] ferments and becomes sour, but the starch that does not undergo fermentation is rendered the more pure by this process’. An acidic solution is added to the swelled grains or flour as it ‘regulates the fermentation, and prevents the mixture from becoming putrid’. Nichelson, furthermore, writes that the acidic solution from former fermentations can be used for this purpose.66 Also Wagner (1860) and Meyer (1888) describe similar fermentation stages. Meyer writes that fermentation raises the starch yield, because it results in destruction of the so-called ‘Kleber’, probably the non water-soluble gluten, which hinders starch extraction.67 Wagner gives a description of the different fermentation stages: the formation of carbon dioxide, which lifts the layer of fermenting flour until it is suspended above the liquid, then alcoholic fermentation, and subsequent stages where in succession acetic acid, lactic acid, then butter acid and sulphuric acid are formed, as well as ammonia.68 According to Rehwald (1911), in a final fermentation stage the mixture produces a foul smell and becomes covered with fungus. To check if the starch is ‘ripe’, a little of the deposit is taken from the jar, mixed with water and decanted by inclination. If after decanting of the starch only a mixture of bran and brown ‘Kleber’ remains, the starch is ready for sieving and cleaning.69

12.5.3 Other raw materials & variations in preparation process

In the eighteenth century, potato starch manufacture starts in France and Germany.70 However, whether this material is suitable for preparatory layers is uncertain. Wagner (1860) writes that potato starch is not suited for book binding and for starching clothes since the larger starch particles will clump up during ironing. He adds that potato starch quickly goes off.71 Interestingly, Carlyle (2001) quotes a nineteenth century author, Bachhoffner, who writes that laundry starch is usually obtained from potatoes.72 Rehwald (1911) still writes that wheat is used most for starch production in Europe, while in South Europe and the United States also corn starch is important as well.73

65 Wagner 1860: 93-5
66 Nicholson 1808: n.p.nrs
67 Meyer 1888, vol 15: 237-8
69 Rehwald 1911: 138-9
70 BeMiller and Whistler 2009: 3
71 Wagner 1860: 95-6
73 Rehwald 1911: 124. Most important for starch glue production nowadays are maize, rice, wheat and tapioca. Köhler 1971: 27.
12.6 Composition of wheat and rye starch

Gomand (2011), writing about modern starch, describes it as consisting mainly of amylopectin (AM) and amylopectin (AP) which is the sticky part of the starch, as well as of small amounts of lipids, proteins, minerals and monosaccharides. In the identification of starches by iodine staining, it is the AM that discolours, while the AP does not discolour.\textsuperscript{74}

AM is built up of glucose units that form long chains, AP consists of similar glucose units with many side chains.\textsuperscript{75} In starch, intermediate molecules may also be present.\textsuperscript{76} The starch gelatinisation temperature varies with the average chain length of the polymers present\textsuperscript{77} and is generally a little lower in rye starches than in wheat starch.\textsuperscript{78} The exact degree of swelling of starch depends on various factors, including the composition of the AM and the AP, but also on the duration of the heating and the stirring method.\textsuperscript{79}

Descriptions of modern starch production methods by BeMiller & Whistler (2009) demonstrate that current methods differ from historical methods. Chemicals are sometimes added to the mixture to facilitate starch extraction and the perfection of extraction methods results in a refined product of more controlled particle size and more pure composition than would have been available historically.\textsuperscript{80} According to Rehwald (1911) early starch production was not fully successful in separating the starch from other constituents of the grain. By the time that Rehwald was writing, methods had been invented that facilitated extraction by ‘destroying’ other components inside the wheat kernel.\textsuperscript{81}

Unlike wheat flour, rye flour does not seem to have been used for starch production on an industrial scale. According to Verwimp et al., quoting Schierbaum et al. 1991, ‘the high content of arabinoxylans with high water-binding and thickening properties and the poor dough forming properties of the rye protein make rye less suitable for industrial processes involved in recovering starch’.\textsuperscript{82}

12.7 Selection of raw materials for the reconstructions

From the above overview of the historical use of cereals and historical starch production, it can be concluded that wheat and rye flour are most likely to have been used historically and that wheat is the most likely source for starch. Historical recipes for starch preparation describe preparation from grains or from flour, according to methods with and without fermentation. In addition, it is clear that historical wheat and rye and their derived starches possibly had had slightly different characteristics than their modern

\textsuperscript{74} Gomand et al. 2011: 2730
\textsuperscript{75} Köhler 1971: 28
\textsuperscript{76} Gomand 2011
\textsuperscript{77} Gomand 2011: 2733
\textsuperscript{78} Nyman, Zeitschr. Unters. Nahr. Genussm. XXIV: 673
\textsuperscript{79} Harris and Jesperson 1946: 479
\textsuperscript{80} See for modern starch production BeMiller and Whistler 2009
\textsuperscript{81} Rehwald 1911: 128, see note 12
\textsuperscript{82} Verwimp et al. 2004: 85
equivalents, as both the raw materials, production processes and refinement procedures differ.

Based on Zeven’s (1990) identification of wheat landraces that were historically grown in the Netherlands, a selection was made of two wheat types for the reconstructions. These were ‘Zeeuwse witte’ belonging to the Zeeuwse landrace group, and ‘Oude Ris’, belonging to the Gelderse landrace group. Both landrace groups are native to the Netherlands, but since they have international ties in different geographical directions, respectively west and south/east, this selection represents a geographical spread that covers a large section of North West Europe. As a rye grain, ‘St. Jans rogge’ (‘St. John rye’), a rye landrace grown since Medieval times in North West Europe, was selected. All these cereals are organically grown.

Although the composition of these cereals is not likely to be an exact copy of the wheat and rye used for historical preparatory layers, they are likely to be more similar to historical varieties than modern and not organically-grown flour types, that may, in addition to different milling methods, have undergone bleaching or may contain additions such as fungicides or flow agents.

Grains were purchased whole and were milled once on a stone grinding mill similar in construction to historical grinding mills. Flour was strained with a stainless steel flour sieve to remove most of the bran. The resulting flours were cream coloured and contained a small portion of darker bran flakes.

12.8 Starch production for the reconstructions

From whole grains, starch was extracted according to a procedure that combines details from the recipes provided by Cato, the Kentucky Housewife and Buc’hoz. These recipes were selected because the procedure is repeated in other sources and remains relatively consistent throughout the period. The grains were soaked for four days in demineralised water, which was replaced every morning and evening. By then, the grains were sufficiently soft to crush between the fingers. On the third day of soaking, some light fermentation was apparent as a yeasty smell and the formation of a light froth on the water surface.

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83 In this context it is important to note that research by Zeven, van Tielhof and Belderok has shown that even in the seventeenth century, the international trade between cereals resulted in the availability of foreign cereals in North West Europe and that also import, export and cross-breeding of different landraces led to international influences.
84 Both wheat types and the rye were produced on an organic farm near the town of Deventer, in the IJssel region of the Netherlands. They are grown in earth on which the farmer practices crop rotation: alternating the production of wheat, spelt, rye, corn or cattle graze. Oral communication Willy Gooiker, Wilp, 8-12-2011.
85 Nitrogen fertilisers not only show up in analyses, but they influence the protein content of the seeds (Campbell 2011). Artificial fertilisers were introduced in the United States and Canada in the second half of the nineteenth century (Belderok et al 2000: 11) and introduced in Europe only at the end of the nineteenth century (Bieleman 2008: 282-4). Therefore their inclusion in these reconstructions is undesirable.
86 As stated above, growing conditions influence the chemical composition of the grains. Moreover, environmental factors have changed greatly since the seventeenth and eighteenth century.
87 Small stone mill with two horizontal granite stones, owned by Willy Gooiker in Wilp, Netherlands. The mill was cleaned with a run of seed before the seed to be employed in reconstructions was milled.
88 See Introduction to this dissertation for an explanation of the use of demineralised water.
The wet grains were crushed with a beech wood pastry roller. The crushed grains were placed inside a linen bag, the bag was filled with demineralised water and squeezed and rinsed to extract the starch. The liquid was collected in a glazed earthenware bowl (Fig. 12.1). During starch extraction, a sticky white material hindered the starch from flowing out. This was probably the ‘Kleber’ described in historical sources.

From flour, starch extraction was executed with all three cereals, using whole meal flours. As recipes for starch extraction from flour generally describe a fermentation stage, the flours were mixed with demineralised water and allowed to ferment at room temperature for seven days. Each of the flours selected underwent the fermentation stages described by Wagner (1860) and Rehwald (1911). Starch was washed out, following the same method with the linen bag as described for making starch from grains. Washing out was easier than with seed starch, as no sticky white gluten (the ‘Kleber’) appeared.

The starches took two days to settle in the water, after which the supernatant water was removed and replaced with fresh demineralised water. During washing, the formation of gas bubbles and an acidic smell in the flour starches demonstrated that fermentation continued. Water was refreshed and the starches were washed three times (Fig. 12.2). After washing, the starches were dried in a Whatman paper filter on a radiator.

The starches extracted from the grains are stark white, while the starches extracted from the fermented flour are more greyish in colour. The starches from fermented flour contain more remnants of the bran and have a stronger odour, slightly sweet and putrid. Rye starches are slightly darker in tone than wheat flour starches. No visible difference is noted between starches extracted from the two wheat flour types.

Figure 12.1 Wringing crushed seeds in linen bag to extract starch

Figure 12.2 Extracted starches settling
12.9 Preparation of the ground reconstructions

Reconstruction canvases were designed to investigate the effect of the most important variations in flour paste and starch paste recipes. Linen canvas was washed 8 times in hot tap water, rinsed 3 times in demineralised water and stretched onto wooden strainers. Glue employed: HART Project, batch 16/2/2012. Preparation details for these sheep parchment glues can be found in Witlox 2008.

Areas to be covered with ground layers received a size layer of 3.5 : 100 (w/w) concentration of sheep parchment glue, prepared from traditional sheep parchment. Glue employed: HART Project, batch 16/2/2012.

Two types of fillers described in historical sources (See Table 12.2 in Appendix 19) were chosen, stack-process lead white (lead carbonate) and pipe clay (kaolin containing clay). Pressed for the HART Project.

As a pipe clay, an unprocessed ball clay was selected of a type that was used for clay smoking pipes and which is quarried from ball clay deposits that were worked in the seventeenth and eighteenth century. The linseed oil used was pressed from the seeds of organically grown Electra flax. Animal glue used in paste recipes was extracted from alum tawed goat’s leather according to historical recipes with an egg substitute.

90 Supplied by Fred Locke, Imerys Minerals Ltd. The clay contains 56 % silicium dioxide, 29 % aluminium oxide, between 1.2-1.7 % iron oxide, 1.6% titanium oxide, 0.3 % calcium oxide, 0.37% magnesium oxide, 3% potassium oxide, 0.5% natrium oxide. Locke provided details on the clay pit in an email dated, December 16 2011.

92 Pressed for the HART Project. See Carlyle 2005

93 similar to ‘glove leather’, see Witlox 2008. A different animal glue was chosen than used for the size layer applied to some canvases, to allow for identification of the individual layers. Glue type analysis is not executed within the present research but may be important in future investigations.
Three types of paste were employed: prepared from sieved flour, pastes prepared from the starch extracted from seeds and from starch extracted from flour. To allow for comparison between the flour pastes, they were all prepared according to the same procedure, in a one to five (w/w) ratio of flour to water (see Table 12.4 in Appendix 19 for preparation details). For starch pastes, a different ratio was employed, one to six (w/w) of starch to water, as tests demonstrated that starch pastes produced from starch are more rigid than pastes made directly from the milled seeds. These proportions result in creamy pastes that are easy to spread with a palette knife. Pastes without glue were prepared in an enameled pan by dispersing flour or starch in cold water with a metal whisk, followed by heating the mixtures on a hot plate while stirring continuously (Fig. 12.4). Upon the thickening of the mixture, half of the paste was removed and used warm, while the remainder was left to boil slowly for fifteen minutes before application. For recipes with animal glue, tepid animal glue (six to hundred w/w) was used for paste preparation instead of cold water. Procedures were the same.

The fillers were prepared prior to mixing with the flour or starch paste. The lead white pigment was ground in linseed oil (self-pressed) using a glass muller on a granite slab. The ball clay was made into a paste using distilled water, the paste was ground using a glass muller on a granite slab to ensure even dispersion of the particles in the medium. The ball clay/water paste was stirred directly into the flour paste. The lead white oil paint was mixed with the paste using a stainless steel spatula on a granite slab, as stirring the paint into the starch did not result in a good mixture.

The resulting pastes were applied to the prepared canvases and to Melinex using a stainless steel spatula (Fig. 12.5). After the starch and flour paste layers had dried, a section of each test area was covered with a grey oilpaint consisting of lead white and carbon black (ground on a granite slab with a glass muller) and applied using a stainless steel spatula. This grey layer was applied to mimic a double ground similar to those advised in historical recipes.

**12.10 Discussion of results of reconstructions**

**12.10.1 Size layers and grounds: working properties and visual characteristics**

Table 12.4 in Appendix 19 provides a complete overview of observations made during preparation and application and Table 12.5 in Appendix 19 provides observations about the characteristics of dried and aged paste grounds.

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94 Melinex: http://www.kremer-pigmente.de RN 75 (thickness 75µ), 105 gram/m²
Reconstructions led to a number of observations. It was very clear that whole meal flour is not a feasible raw material. Both as a size layer and as a ground binder, the bran flakes make the pastes impossible to spread evenly. Stripes appear within the layer as the larger particles are dragged through the still soft paste and give a very uneven result (Fig. 12.6).

The wheat flour/starch paste slightly thickens if left to boil longer, but the rye pastes become thinner in consistency. As a result, long-boiled rye pastes have a consistency of fluid yoghurt instead of the creamcheese consistency seen in wheat pastes. The rye pastes cannot be spread using a spatula without drips forming while the paste is carried to the support. A brush application seems more likely for such pastes.

Pastes made from starch result in more transparent, slightly more glossy size layers than the pastes made with flour. Applied as ground layers (with lead white or ball clay), all pastes have matte or, in the case of grounds with a fifteen to hundred part addition of linseed oil, have a velvety surface.

Boiling time influences crack formation in the ground layers: a comparison between paste heated until thickening and paste boiled for an additional fifteen minutes demonstrates that longer boiling result in a lower degree of cracking (Fig. 12.7). An explanation may be the fact that continued boiling leads to water evaporation, and cracks may be the result of contraction upon evaporation of water. Whether this factor accounts for this difference or if breaking-down of the starch molecules by heat results in less contraction, is uncertain.

Crack formation occurs primarily in thickly applied layers. There does not seem to be a relation between crack formation and flour or starch type.

Additions tested include animal glue and linseed oil. Animal glue additions significantly influence the working properties of the pastes. They become stiff upon cooling, as the animal glue content forms a gel. Emulsified mixtures with linseed oil are very lumpy and
difficult to handle if not kept at an elevated temperature. This may be an important factor when considering the preparation of large supports.

A 3 parts (by weight) addition of linseed oil to hundred parts of paste has little effect on the paste characteristics: they similarly to pastes without oil and the dried layers are almost impossible to distinguish visually from those prepared without linseed oil. An addition of fifteen parts of oil to hundred parts of paste however, markedly changes the character of the paste, which has a silky, somewhat slippery feel and spreads beautifully. These dried pastes have a darker tone and look more saturated and velvety. The pastes develop a halo of oil binder which bleeds out into the surrounding canvas and which will also bleed through to the reverse if no size layer is present. If a size layer is present, bleeding through to the reverse is absent everywhere, with the exception of the section with sieved rye flour and animal glue paste, to which after fifteen minutes boiling, fifteen weight parts of linseed oil have been added.95

Pastes without glue or with fifteen weight parts of oil visibly absorb oil from the linseed oil bound grey layer applied on top. In pastes of pipe clay and flour paste with starch additions, a halo appeared in the underlying paste-bound layer (Fig. 12.8).

During sampling, the rather brittle nature of pastes without oil is clear. Glue-bound pastes are more hard and resistant to the scalpel than pastes without glue.96

12.10.2 Examination of reconstructions in cross section with light microscopy; results of potassium iodine staining

Photographs of all cross sections before and after iodine staining are found in Appendix 19, Table 12.7.

The most important observation from the investigation of cross sections is the fact that there is no clear indication in visible light and with UV radiation of the presence of the starch or flour binder in either the size layer or the ground layers sampled.97 In visible light, both lead white and pipe clay based layers reveal features that may also be associated with oil and glue bound layers (Figs. 12.9 a-e). Ball clay based layers look similar to chalk and glue or chalk and oil ground layers: no distinct particles of starch can be identified, the layer has a light beige tone, with often a slightly more saturated section at

95 Section 39b in Table 12.5
96 With such hygroscopic layers, brittleness is expected to be dependent on the relative humidity. The rooms where samples are stored has a relatively constant RH of ca. 50%, as it is inside a building climatized for museum objects.
97 This confirms observations based on reconstructions of 19th century recipe by Carlyle et al. 2008b: 126
the top. The higher saturation of this section appears not to be related to starch concentration (more paste binder), as it does not stain more than the rest of the layer. Examination under UV radiation shows that flour pastes demonstrate a bluish fluorescence, which seems stronger in samples that contain 15 weight parts linseed oil. Artificial ageing of samples has not resulted (so far) in marked differences in the intensity of fluorescence.

It is only by staining with the potassium-iodine stain that the presence of starch or flour reveals itself. No starch granules can be seen in the stained cross sections taken from the reconstructions, as they are destroyed during the paste preparation. However, even in animal glue bound pastes with an addition of fifteen weight parts of linseed oil the flour or starch is still stained by the potassium-iodine stain.

As only the areas that have a high binder ratio are stained, e.g. areas in between particles, the staining pattern shows the division of binder in ground layers. In clay containing samples, these areas seem to have a laminar orientation, parallel to the canvas (See Fig. 12.9b). In samples with an oil addition, the binder-rich regions are relatively short and seem less horizontally oriented (Fig. 12.9c). Also samples containing lead white reveal horizontal bands of binder. Here the distribution of starch is more varied. Some samples do not exhibit very strong horizontal bands, while others clearly do so (Figs. 12d, 12e). Possibly the pressure applied by the spatula during application results in particle orientation. This would explain the difference observed in the samples removed from the reconstructions containing clay and lead white. These differences clearly relate to pigment morphology: clays have a plate-like structure and lead white particles have a more rounded form. Monitoring of the samples during ageing will reveal if the lamellar structure influences delamination patterns.

While differences in the degree and colour of the Lugol stained section (brownish or blackish) are noted, comparison between different variables does not reveal a pattern that can be related to composition.

12.11 Conclusions and suggestions for future research

This study demonstrates that flour and starch pastes, applied in thin layers so as to prevent crack formation, can be used for canvas preparation. Both the pastes containing lead white and ball clay as fillers/pigments meet the requirements of a preparatory layer that were formulated in historical sources: these pastes fill the canvas interstices, fix the loose canvas fibres and provide a base tone. In case more saturated layers are required, the water and flour paste can be mixed with animal glue, some linseed oil can be added, or they can be covered with an oil-bound second ground layer.

Only short-term artificial ageing was included in this study. The fact that historical recipes discuss adhesion problems associated with the hygroscopic nature of flour and starch, suggests that flaking may become a problem under changing climatic conditions. The

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98 Particle orientation parallel to the canvas also seems evident in reconstructions of ball clay containing flour paste layers executed by Carlyle. Carlyle et al. 2008b: 127, figure 6a.

99 See Vibert 1892: 96-8 for a description of the function of a ground layer, see also Chapter 2.
behaviour upon ageing of the reconstructions produced for this study will be monitored in the future. Particular attention will be paid to the question whether flaking patterns are associated with the lamellar structure within flour paste ground layers.

Microscopic examination of cross sections of the reconstructions confirm earlier work (Carlyle et al. 2008b) which demonstrated that paste binders are not easily distinguished under visible viewing conditions from other binders. While staining or instrumental analysis allows for the identification of flour or starch, the presence of these materials is not regularly investigated in the analysis of cross sections of ground layers. It is hoped that this study, which has assembled many historical recipes advising the use of flour and starch for preparatory layers, will result in more attention for these materials. Only investigation by instrumental analysis will answer the question whether flour and starch were employed on a regular basis in grounds for oil paintings. Their hygroscopic nature may require more strictly regulated environmental conditions and may necessitate a special approach during conservation treatments, therefore knowledge of the use of starch or flour paste is important for the conservation field.

100 Instrumental analysis by GC-MS of the starches will be the topic of a future publication that addresses two questions: whether there is a difference between starch produced according to historical recipes and modern starch, and how starch that appears in complex mixtures (in this case: flour, glue and oil) are best identified.
Table 12.9a

<table>
<thead>
<tr>
<th>Bright field image</th>
<th>UV image</th>
<th>Iodine stained x-section</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 12.9a</td>
<td>Composition: sieved Oude Ris flour size layer, long boil</td>
<td></td>
</tr>
<tr>
<td>Figure 12.9b (Artificially aged)</td>
<td>Composition: No size layer, Oude Ris seed starch, pipe clay, short boil</td>
<td></td>
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<tr>
<td>Figure 12.9c (Artificially aged)</td>
<td>Composition: No size layer, rye seed starch, pipe clay, 15% (w/w) linseed oil, short boil</td>
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<tr>
<td>Figure 12.9d (Artificially aged)</td>
<td>Composition: Animal glue size layer, Zeeuwse Witte seed starch, lead white in oil, animal glue, short boil</td>
<td></td>
</tr>
<tr>
<td>Figure 12.9e (Artificially aged)</td>
<td>Composition: Animal glue size layer, sieved Oude Ris flour, lead white in oil, animal glue, short boil</td>
<td></td>
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