Ancient Monuments Laboratory
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THE ANALYSIS OF PAINT SAMPLES FROM HAMPTON COURT, MIDDLESEX.

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Summary

Post medieval paint samples were analysed using the Scanning Electron Microscope, including backscattered imaging. The results showed a transition from lead based to titanium white paints.

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The Analysis of Paint Samples From Hampton Court, Middlesex

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1 Introduction

Cross-sections of paint were taken from different rooms and different locations within rooms and analysed to determine the decorative history of the rooms. Sampling and optical analysis was carried out by Helen Hughes (PIC DA). The pigments used in the coloured layers were identified mainly by optical microscopy. A large number of the paint layers were white or off-white and differences in pigments could not be determined by optical microscopy. There have been three significant changes in the white pigments used in paints, from lead white to barium sulphate to zinc sulphide and finally to titanium dioxide. The changes are shown in Table 1 (extracted from a list compiled by G.L. Martin of the Conservation department of the Victoria and Albert Museum in 1984). By detecting these changes of composition in the paint cross-section approximate dates for certain paint layers could be determined, and with the aid of documentary evidence some firm dates could be established for the decorative history of the rooms. This data enables re-creation of the decorative design of a particular room at a given date.

Table 1 The Sequence of Pigments in White Paints

Pigment	Approximate Date of Introduction
$2PbCO_3.Pb(OH)_2$	
ZnO	1750
$2PbCO_3.Pb(OH)_2 + BaSO_4$	1820
$BaSO_4$	1820
$ZnS+BaSO_4$ (Lithopone)	1850
ZnS	1850
TiO_2	1916-1919

2 Sample Type and Preparation

The samples were flakes of paint removed from wooden surfaces, which in some cases showed the complete surviving sequence from wood to the most recent paint layer. The problem of unconformities between paint layers has not been investigated. It is generally assumed that removal of earlier paint layers was not carried out prior to repainting. The samples were mounted on edge in cold setting resin and polished to a one micron finish. Optical analysis was undertaken to determine the coloured pigments used and then the sections were carbon coated for examination using the Scanning Electron Microscope (SEM). Elemental analyses were obtained using an energy dispersive X-ray analysis system, and the imaging utilised the back-scattered electrons thus obtaining enhanced atomic number contrast (high atomic numbers are white on the photographs, and low atomic numbers

dark).The methods of analyses are briefly discussed in the report on the analysis of paints from Osborne House (McDonnell 1989).

3 Results

3.1 HC/12/33

This section showed that there were three types of white pigments used (Plate 1). In the first period the paints were lead based (Table 2, layers 1 - 5, white layers at top of picture in Plate 1). In layer 6 barium sulphate was introduced in small quantities (therefore post 1820), and in layer 7 zinc was added and the amount of lead significantly reduced (post 1850). In layers 8 - 10 the lead had been replaced with barium and zinc (dark grey layers at bottom of Plate 1). In layer 11 titanium was introduced and the barium reduced, but zinc was retained (post 1919). In layer 12 barium was absent. The optical study identified a red priming layer on the wood, but this was not identified under the SEM, although iron (and aluminium) were detected in the upper surface of the wood. A dark brown layer was also identified mid-way through the sequence and is therefore layer 7, which had a high iron content (black layer between white and grey layers in Plate 1).

Table 2 Elements Present in Each Layer of Sample HC/12/33
Layer 1 = basal layer. Layer 12 = most recent paint * = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements	Dates
1	m		m					*	Al	
2	m							*	Al	
3	m							*	Al	crack between
4	m							*	Al	3 and 4
5	m							*	Al	
6	m		m				m	*	Al	1820+
7	m	*	*		*	m	*	m	Al	1850+
8	m	*				*	*		Al	
9	m	*				m	*		Al	
10	m	*				*	m		Al	
11	m	*		*		*	m		Al	1919+
12		m		*		*			Al	

A similar sequence to HC/12/33 was present in sample HC/12/21/62 (Plate 2). The first sequence of paint layers were lead based (Table 3, Layers 1 - 6, white layers in bottom half of Plate 2). There were two distinct layers identified by using BSE within this sequence, both showing black, ie lower mean atomic number (Z) in contrast to the lead based paints. The first was layer 2, which had a high copper content, and layer 4 which was high in aluminium with calcium and sulphur also present. Barium, zinc and sulphur wholly replaced lead in layer 7 (post 1850). Layer 8 was dark under BSE and only zinc was detected (black layer below grey/white layers in top of Plate 2). In layer 13 titanium was introduced (post 1919), and in layer 14 it had wholly replaced zinc and barium. Magnesium was present in the most recent layer.

Table 3 Elements present in Each Layer of Sample HC/12/21/62
Layer 1 = basal layer. Layer 15 = most recent paint * = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements	Dates
1	m		m					*	Al	
2	m		*		m			*	Al,K,Cu(*)	
3	m		*					*	Al	
4		*?	m					m	Al(*)	
5	m							*	Al	
6	m							*	Al	
7	m	*	m			*	*		Al	1850+
8						*				
9	m	*	m			*	*			
10	m	*				*	*		Al	
11	m	*	m			*	*		Al	
12		m				*	m		Al	
13	m	*	*	*		m			Al	1919+
14			m	*						
15	m			*					Mg,Al	

3.3 HC/12/21/63

All the paint layers were lead based,(therefore all are certainly pre-1919 and possibly pre c. 1850) except for a coloured layer mid-way through the sequence (Table 4 layer 3) which contained calcium, sulphur and copper as major elements, and could be equated with layer 2 in sample HC/12/21/62.

Table 4 Elements present in Each Layer of Sample HC/12/21/63

Layer 1 = basal layer. Layer 5 = most recent paint
* = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements Dates
1	m		*					*	Al(*)
2	m							*	Al
3	m	*	*		m			m	K, Cu(*)
4	m		m					*	Al
5	m		m					*	pre-1919

3.4 HC/22/21/74

Sample HC/22/21/74 (Plate 3) was characterised by a large number (17) of lead based paint layers, and relatively few (2) more recent layers (two uppermost layers in Plate 3). This may be due to the stripping back of the latest layers, since no titanium was detected. The first layer was a red priming layer (Table 5, layer 1) with a small level of lead present. Layers 2 - 17 were predominantly lead whites, but some layers (3,5 and 7) contained inclusions, probably of calcium sulphate. In layers 13 - 15 large inclusions of barium (sulphate?) were also present (post 1820). Layers 16 contained lead, barium and zinc (post 1850), but was dark under BSE (black layer between uppermost grey layers and white layers in Plate 3), and layer 17 contained only lead and zinc. Lead was absent from layers 18 and 19.

Table 5 Elements present in Each Layer of Sample HC/22/21/74

Layer 1 = basal layer. Layer 19 = most recent paint
* = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements	Dates
1	m		m		m			m	Al (ochre?)	
2	m							*		
3	m	*	*					*	Al	
4	m							*		
5	m	*	*					*	Al	
6	m							*		
7	m	*	*					*	Al	
8	m							*	Al	
9	m							*		
10	m							*		
11	m							*	Al	
12	m		m					*		
13	m							*		
14	m		m				m	*		1820+
15	m							*		
16	m	*	m			m	m	*	Al	1850+
17	m					*		*	Al	
18	m	*				*	*		Al	
19	m	*				*	*		Al	pre-1919

3.5 HC/61/3/10

In Sample HC/61/3/10 had lead and zinc based paints with some barium present in 4 layers, but no titanium based paints. There were 7 layers of lead based paints (layers 1,3-8, Table 6). Layer 2 was dark under BSE and contained only calcium and sulphur as major elements. Barium was present in layers 3 and 4 (post 1820). Optical analysis had shown that there were some weakly coloured layers within the lead based paints, but these could not be distinguished during the SEM analysis. This shows that the coloured paints were predominantly lead whites with the addition of small quantities of other (colouring) pigments. Further detailed study might be able to identify small inclusions of other pigments. It was noted that phosphorus was present in five layers, and aluminium was less common than in most of the other specimens examined. Zinc was introduced in layer 8 (post 1850), and layers 9 - 14 were predominantly zinc based, with barium present in two layers (11 and 13). The most recent layer (15) was an aluminium silicate.

Table 6 Elements present in Each Layer of Sample HC 61/3/10
Layer 1 = basal layer. Layer 15 = most recent paint
* = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements	Dates
1	m		m					*	Al,P	
2	m	*	*					m	Al,	
3	m						m	*	P	1820+
4	m		m				m	*		
5	m							*	P crack between	
6	m							*	P 5 and 6	
7	m							*		
8	m	?				m		*	Al,P	1850+
9	m					*				
10	m	m	m			*				
11	m	*				*	*			
12		m				*				
13	m	*				*	*			
14		m				*			Cl	pre-1919
15	*		m			m			Al(*)	recent

4 Conclusions

The summarised results from the analyses of the Hampton Court samples are given in Table 7 . They demonstrate that no two samples are exactly the same, although general trends can be observed. There are only two samples that have titanium based layers of paint, and one of which has been overpainted by a modern paint.. The mixed layers vary from sample to sample, but show a general trend that barium preceded the use of zinc, which continued on after the use of barium had ceased.

Table 7 Summary of Results. Number of Paint Layers Identified for Each Paint Type

Sample	Pb Based	Mixed Pb/Ba/Zn	Ti Present	Mg/Al/Si Based
HC/12/33	5	5	2	-
HC/12/21/62	6	6	2	1
HC/12/21/63	5	-	-	-
HC/22/21/74	13	6	-	-
HC/61/3/10	2	13	-	-

Reference

McDonnell G 1989 The Analysis of Paint Samples from Osborne House, Isle of Wight.
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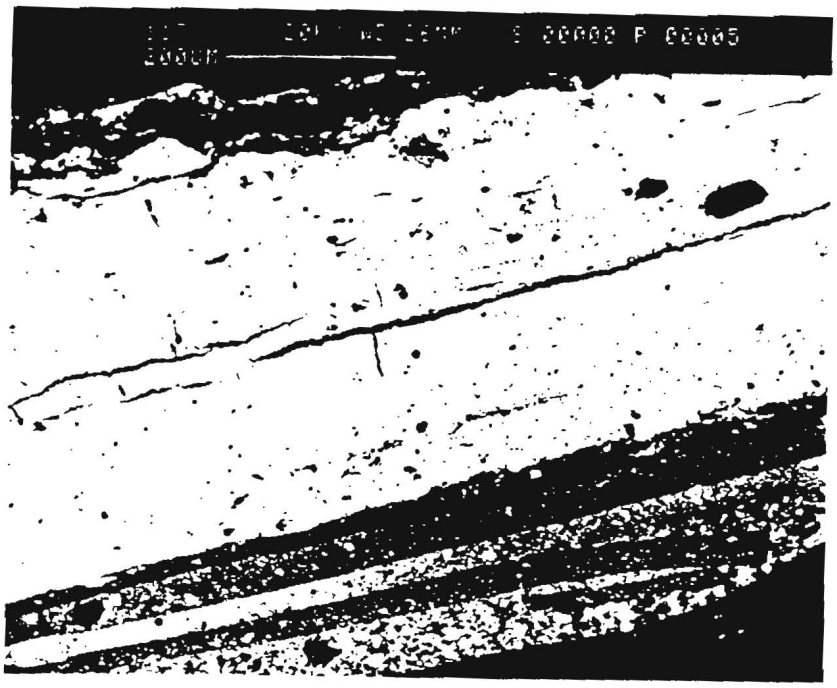

PLATE 1 Sample HC/12/33 BSE Image of Whole Section
(lead based paints - white; most recent layer - bottom of picture)

PLATE 2 Sample HC/12/21/62 BSE Image of Whole Section
(lead based paints - white; most recent layer - top of picture)

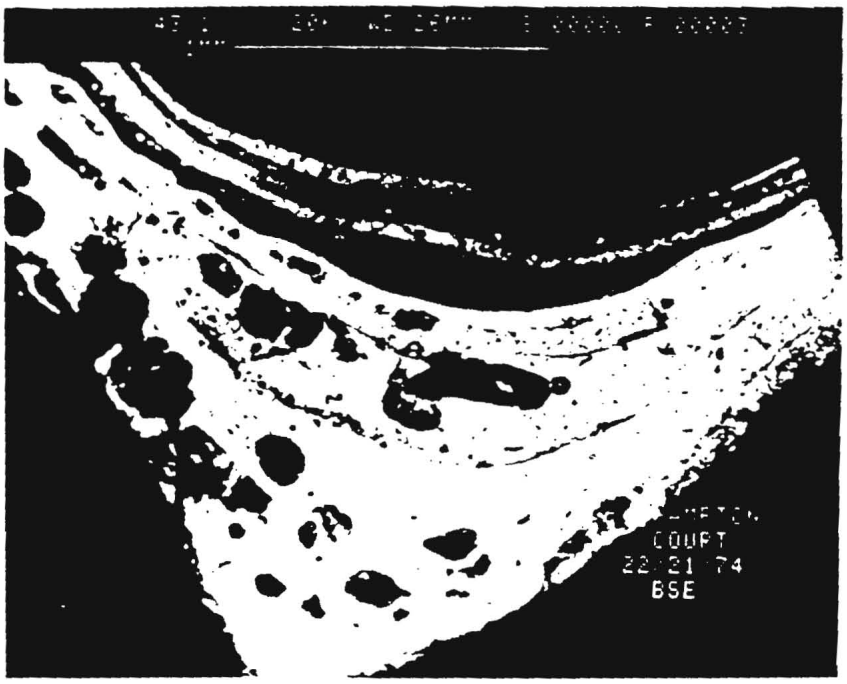

PLATE 3 Sample HC/12/21/74 BSE Image of Whole Section (most recent paint layer - top of picture)