Ancient Monuments Laboratory
Report 127/89

THE ANALYSIS OF PAINT SAMPLES FROM OSBORNE HOUSE, ISLE OF WIGHT.

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Summary

Cross-sections of paint samples from Osborne House (which was built in the 19th century) were analysed using the Scanning Electron Microscope in the Back Scattered Electron mode and with energy dispersive X-Ray analysis. The results show that the pigment used in the white paint changed from lead based to titanium based, with an intervening period in which several different pigments were used, including zinc and barium compounds.

Author's address :-

J G McDonnell BTech PhD MIFA

Ancient Monuments Laboratory
English Heritage
23 Savile Row
London
W1X 2HE

The Analysis of Paint Samples From Osborne House, Isle of Wight

Dr Gerry McDonnell

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 allows 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 mounted paint samples were carbon coated for examination using the Scanning Electron Microscope (SEM, a Cambridge S200 with attached Link energy dispersive X-ray analysis system, using 20KV accelerating voltage).

3 Method of Analysis

The purpose of analysis was to identify the layer(s) at which changes in pigment had occurred. As Table 1 shows they were not clean distinct changes but new pigments were adopted over a period of time. The SEM with an attached energy dispersive X-ray analysis system is one of the best instruments for detecting these changes. However there are two main problems. The first is that the sulphur K peaks overlies the lead M peaks (Figure 1), and the second is that the barium $L\alpha^1$ and $L\beta^1$ peaks overlie the titanium K peaks. This means that it is difficult to positively confirm the presence of sulphur if lead is present, and similarily the presence of low levels of titanium cannot be confirmed if barium is present. The barium $L\beta^2$ do not overlie the titanium peaks but they are very weak (Figure 2), and therefore difficult to use with confidence. Therefore, although X-ray mapping might appear to be a suitable method the peak overlap is a serious problem in positively identifying the elements of interest here.

A second technique was therefore used in conjunction with X-ray analysis. When an electron beam impinges on a sample several effects occur, which includes the generation of secondary electrons (which are normally used to form the image) and X-rays (used for elemental analysis). A third effect is that of Back Scattered Electrons (BSE), which are beam electrons that are reflected back by the sample. These are detected by a diode detector placed above the sample (the electron beam passes through a hole in the centre of the detector). The BSE effect is very susceptible to atomic number (Z) contrast and therefore offer a method of distinguishing between layers based on lead (Pb, Z=82), barium (Ba, Z=56), zinc (Zn, Z=30), titanium (Ti, Z=22) and sulphur (S, Z=16), or combinations of pigments containing these elements. For compounds or mixtures it is the difference in the mean Z value (Table 2) that is detected. High mean atomic number layers appear lighter in the plates than those with lower mean atomic number values.

The combination of both techniques (elemental analysis and BSE imaging) provides the most effective method for studying the paint sections. Examples of both techniques are given in Plates 3 - 5, and the details in Section 4.1.

Table 2 Composition and Mean Atomic Numbers of White Pigments

Pigment	Composition	Mean Z
Flake White	$2PbCO_3.Pb(OH)_2$	68
Barium White	$BaSO_4$	36
Zinc White	ZnO	26
Titanium White	TiO_2	16

4 Results

4.1 Sample OSB.W/15

Analysis showed that there were three groups or types of pigments used (Plate 1). The elements present in each layer are given in Table 3. The earliest phase was a lead based paint layer (Layer 1). During the second phase (Layers 2 - 10, post 1820, Plate 2) mixed pigments were used, these included compounds of lead, zinc and barium. The third group is defined by the introduction of titanium (Layer 11, post 1916-19), when it was used in association with lead until Layer 14. The distribution of elements Pb, Zn and Ti between Layer 4 (bottom of picture) - Layer 16 (top of picture) are shown in Plates 3-5 (white dots indicate the presence of X-rays). These Plates are split showing the BSE image on the right and the X-Ray distribution map on the left. Plate 3 shows the lead distribution analysed using Pb L X-Rays to avoid the peak overlap between lead and sulphur. The dot map shows high concentration of lead in the lowest layer (Layer 4), an absence of lead in the upper titanium layers, and varying concentrations in the mixed layers. Plate 4 shows the distribution of zinc which is concentrated in the lower layers of the mixed layers (Layers 5 - 10). Plate 5 shows the titanium distribution (upper layers), but due to peak overlap the presence of barium in the mixed layers is also detected. The most recent layers are based on titanium only (Layers 15-21), except for the last layer (Layer 21), which was characterised by the presence of a high magnesium content. Silicon and calcium are present in the majority of layers. Other elements are occasionally present, in particular potassium and aluminium. The later was present as a major component in Layers 13 and 15. The presence of chlorine (noted intermittently from Layer 14 onwards) can be the result of either degradation or as a contaminant in the original pigment.

Table 3 Elements present in Each Layer of Sample OSB.W/15

Layer 1 = basal layer. Layer 21 = most recent paint
* = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements & Date
1	m							*	
2	m	?	m			m		*	1850+
3	m		m				m	*	
4	m					m		*	
5	m	?			m	*	m	*	
6	m	?				m		*	
7	m	m	m			*	m	m	K(m)
8		*				*	*	m	
9	m	m				*			
10	m	?				m		*	
11	m	?		m				*	Al(m) 1919+
12	m	*		m				*	
13	*	*		*				m	Al(*)
14	m	m		*	m			m	Cl(m)
15	*	m	m	*					Al(*),K(m)
16	m		m	*					Al,Cl(m)
17	m		*	*					
18		m	m	*	*				Cl(*)
19	m	m	m	*					Al(m)
20	m	m	m	*					Cl(m),
21	m	m	*	m	m				plus Mg(*),Cl,K(m)

4.2 Sample OSB.W/22

This section also showed three types/groups of pigments were used to paint the room (Plate 6, titanium based paints = dark grey layers at bottom of picture; mixed layers = grey layers; lead based paints = white layers; putty = dark grey layer at top of picture). The first was predominantly lead based, but with layers with calcium and iron present (see Table 4). The first layer in the second group of paints (Layer 6, post 1820) contained barium rather than zinc as in sample OSB.W/15. The layers in this group (Layers 6-12) were still predominantly lead based but with barium and/or zinc also present (except for layers 7 and 9). Iron was present in all these layers. Titanium was introduced in Layer 13 (post 1916-19), but zinc and barium continued to be used until Layer 18. From Layer 19 onwards the paints were titanium based except for the final layer (Layer 22) which contained a high level of magnesium as was the case in OSB.W/15.

Other elements were present as was described for sample OSB.W/15

Table 4 Elements present in Each Layer of Sample OSB.W/22 Layer 1 = basal layer. Layer 22 = most recent paint * = major element m= minor element ?=assumed presence

Layer	Si	S	Ca	Ti	Fe	Zn	Ba	Pb	Other elements	Dates
1	m							*	layer below putty	
2			putty layer							
3	m		m					*		
4	m		m		m			*		
5	m		m		*			*	Al,K(m)	
6	m		m		m		*	*		1820+
7	m	(?)	m		*			m		
8	m		m		m	m		*	Al(m)	
9	m	(?)	m		*			*	Al(m)	
10	m	*	m		*	m	*			
11	m	*			*	m	*	m		
12	m	(?)	m		*	m		*		
13	*		m	*	*			*	Al(m)	1919+
14	m	m	m	m	*	m		*		
15	m	m	m	*?	m	m	*	*	Al(m)	
16	m	m(?)	m	*				m	Al(m)	
17	*	*	m	*?	m		*	m	Al(m)	
18	m	*	m	*?	*		*	m	Cl(*)	
19	m		*	*						
20	m	m	m	*					Al,Cl(m)	
21	m	m	m	*	m				Al(*),Cl(m)	
22	m	m	*	m	m				Mg(*)	

5 Conclusions

The results are summarised in Table 5 and show that the two specimens have a similar sequence with few layers based purely on lead, but a large number of post-1919 layers. Both sections terminate with a Mg/Al/Si based paint.

Table 5 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
OSB.W/15	1	9	11	1
OSB.W/22	4	7	10	1

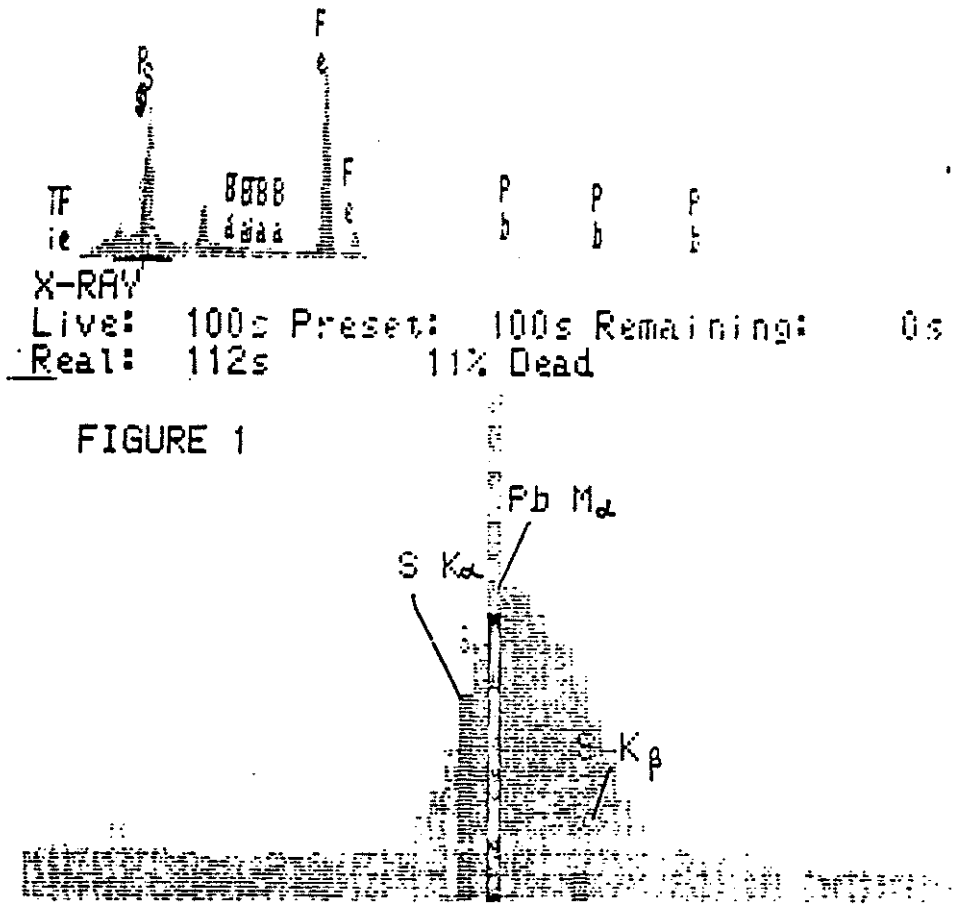
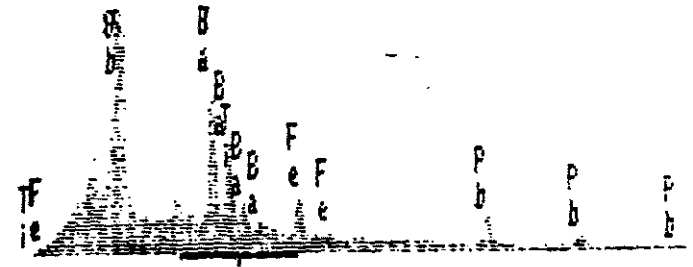

X-RAY
Live: 100s Preset: 100s Remaining: 0s
Real: 112s 11% Dead
Pb Mα
S Kα
Kβ
< 1.700 2.340 keV 2.980 >
CH 127= 1134 CTS
MEM1:OSB22 Pb/S Peak Interference

FIGURE 1



X-RAY
Live: 100s Preset: 100s Remaining: 0s
Real: 122s 18% Dead

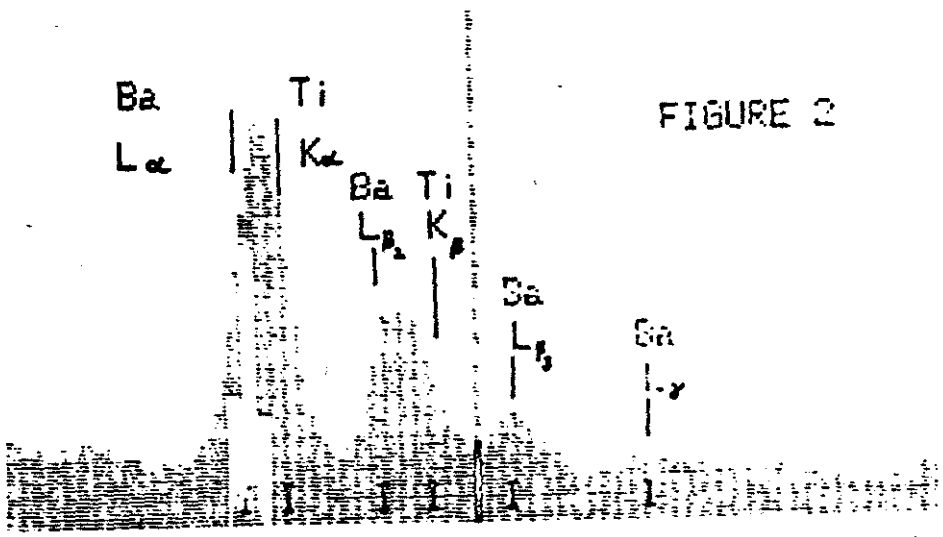


FIGURE 2

< 3.780 5.060 keV 6.340 >
FS= 2K CH 263= 332 CTS
MEM1:OSB22 Ba/Ti Peak Interference

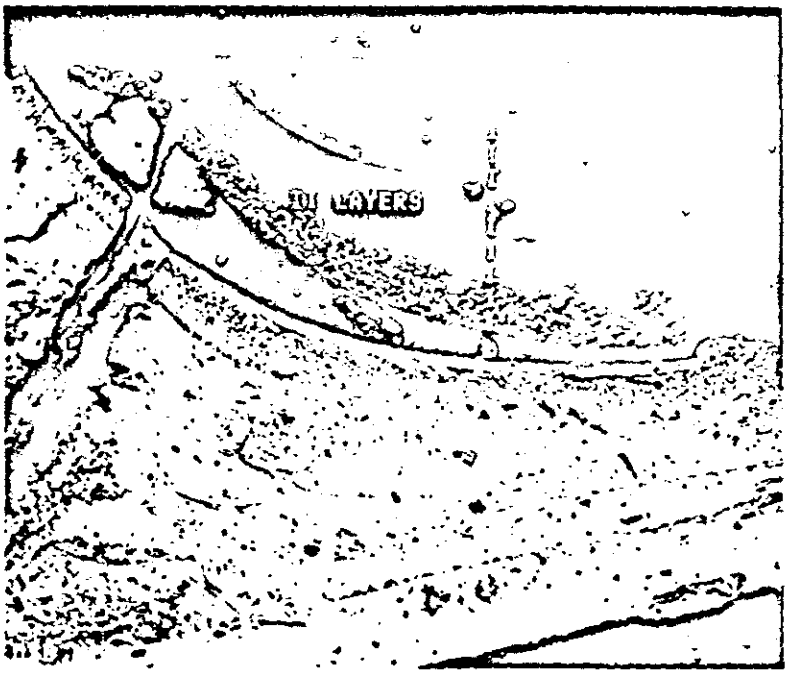


PLATE 1 Sample OSB.W/15 BSE Micrograph Showing the Three Types of Paint Pb based (white), Mixed Pigments (grey), Ti based (dark grey).

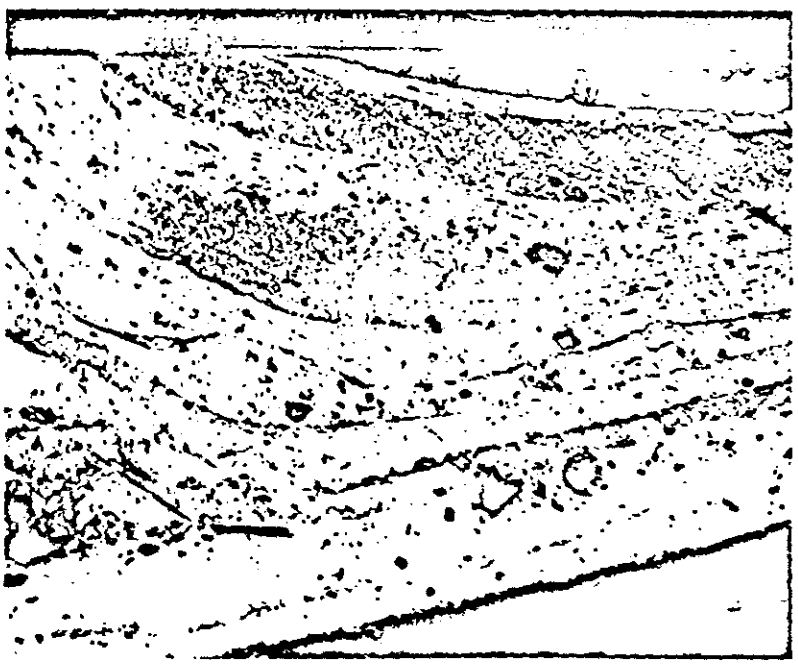


PLATE 2 Sample OSB.W/15 BSE Image of Pb based Paint layers and Mixed Pigment Layers. (Variations in contrast are due to variations in composition, white = high atomic number; black = low atomic number).

PLATE 3, 4 and 5 Sample CSB.W/15 X-Ray Dot Map/BSE Image. Bottom of Picture Pb based Paints, centre mixed pigments, top Ti based paints.

PLATE 3
Pb L X-Ray Map

PLATE 4
Zn K X-Ray Map

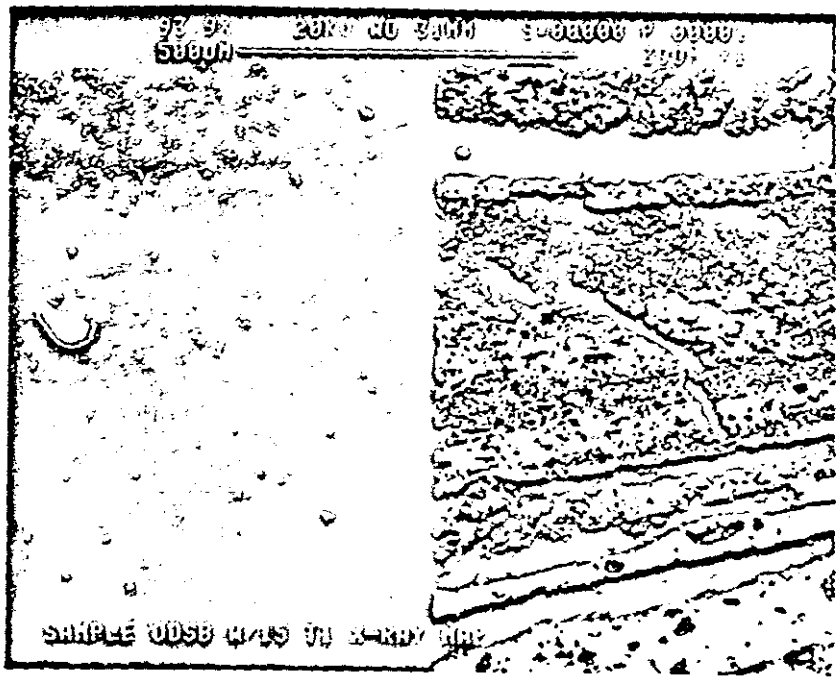


PLATE 5 Ti K X-Ray Map and Ba L X-Rays

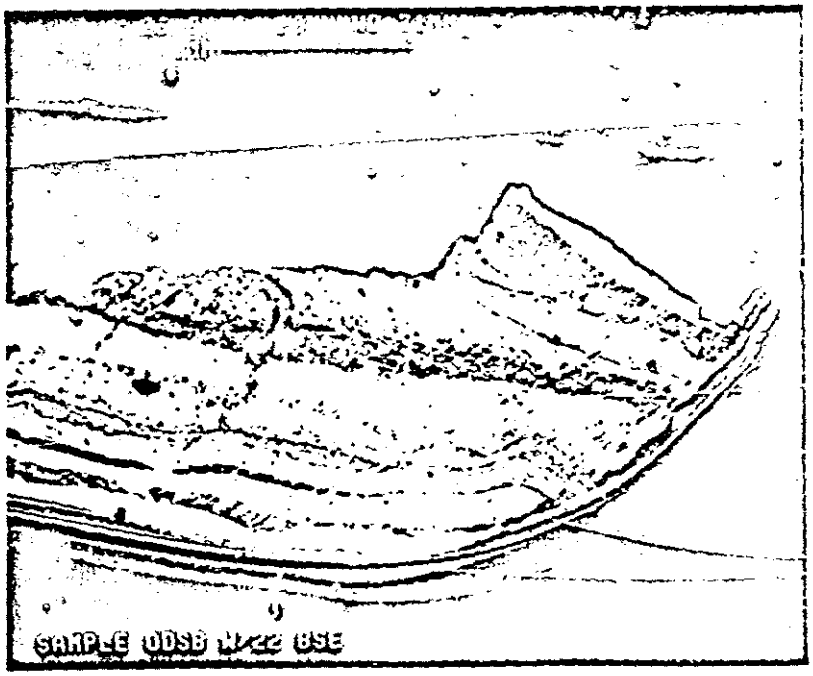


PLATE 6 Sample OSB.W/22 BSE Image of Whole Section. (Bottom paint layers (dark grey) Ti based; centre mixed pigments (light grey); top Pb based (white layers, [the dark grey layer between the two white layers is putty])