Figure 1. Detail showing the lower center of the PMA console table. The areas of gesso loss have been sized with 15% bismuth oxide W/V in stock rabbit skin glue in preparation for gesso fills.

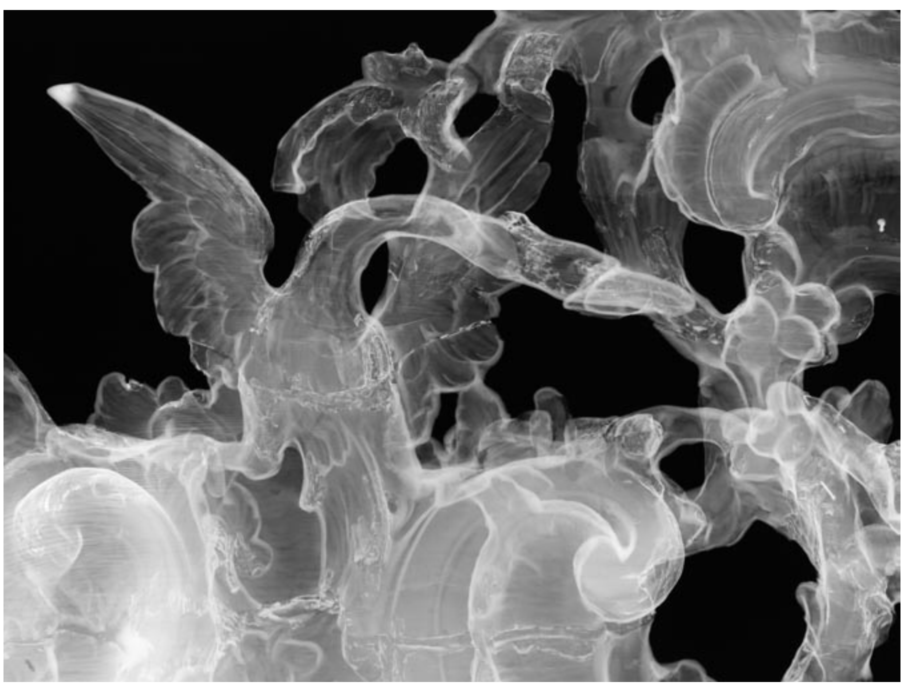

Figure 2. The bismuth oxide sized areas in figure 1 are clearly discernible in this x-radiograph.

Formulating Gesso Fills with Bismuth Oxide for Discrimination by X-radiography

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ABSTRACT

This paper discusses investigation of the use of different gesso formulations and techniques to allow the discrimination of fill materials from the original gesso. Test panels were prepared to observe the effects of pigment composition and gesso thickness on the appearance of x-radiographs. The first test panel was prepared using twelve gessoes formulated with varying proportions of calcium carbonate (Ca CO_3), zinc oxide (ZnO), and bismuth oxide (Bi_2O_3). The zinc and bismuth pigments were chosen because they are stronger x-ray absorbers than the traditional calcium pigments such as calcium carbonate and calcium sulfate (Ca SO_4), which are widely available and inert. Additional tests were carried out to investigate gesso formulations based on calcium sulfate and to assess the effect of a bole layer. The paper will discuss the results obtained from the test panels as well as from the gesso fills used in objects.

Introduction

We have been developing modified gesso fill materials that can be distinguished from original gesso on gilded objects by using x-radiography. In 2002, we reported that bismuth oxide (Bi_2O_3) and zinc oxide (ZnO) could be added to a calcium carbonate ($CaCO_3$) gesso in rabbit skin glue to impart greater x-ray density (Salimnejad, WAG Postprints 2002 AIC Conference). After evaluating a number of gesso formulations containing these oxides, we found that 10% bismuth oxide, 35% zinc oxide and 55% calcium carbonate in rabbit skin glue (RSG) exhibited the greatest increase in x-ray density without adversely affecting the working properties of the modified gesso material. This formulation was applied successfully to an 18th century French console table at the Philadelphia Museum of Art (PMA), and the fills were discriminated easily from the table's original gesso by x-radiography. In this paper, we present photographic documentation (figs. 1–5) of this earlier work as well as our recent studies on the use of bismuth oxide alone in several other traditional gesso materials.

Objectives

In our earlier work, the modified gesso fills were tailored for the treatment of the 18th-century French console table. In several areas of the console table, the gesso lacked colored bole and was exposed due to wear. Therefore for this console table, zinc oxide pigment was used to make the bismuth oxide-modified gesso fills whiter in appearance, and more compatible with the color of the original gesso. On the other hand, for many other objects with colored boles and intact gilding, the addition of zinc oxide would not be necessary. Consequently, one of our objectives in this study was to determine if gesso fills modified with Bi_2O_3 pigment alone could be discriminated from original gesso by x-radiography.

Since we had confined our earlier study to only one type of gesso material, calcium carbonate, our second objective was to determine how other types of commonly used gesso materials would behave in x-radiography studies. Accordingly, this investigation included both the calcium carbonates and sulfates as listed in Table 1. In addition to these materials, we also examined the performance of English China clay,

Figure 3. Detail showing the lower center of the PMA console table. The areas of gesso loss have been sized with 15% bismuth oxide W / V in stock rabbit skin glue and filled with (50%–35%–15% calcium carbonate- zinc oxide-bismuth oxide) gesso.

a white, kaolin clay that is favored as an additive to gesso by some conservators and gilders.

Lastly, in our earlier work we observed that precipitated barium sulfate ($BaSO_4$) did not perform well. Even at relatively low concentrations, the working properties of the $BaSO_4$ gesso suffered and the x-ray density did not change appreciably over a range of concentrations (up to 20%). As a result, our third objective was to examine a different source of $BaSO_4$—blanc fixe, mined— to see if a better performance could be achieved.

Materials and Methods

Two test panels were prepared. Each panel consisted of a ¾″ x 14″ x 18″ Medex® board on which were routed 12 parallel tapered mortises. Each mortise was made to be gradually deeper when moving from right to left along the length of the mortise, with the shallow end being 1/16″ deep and the lower end being ¼″ deep. The mortises were numbered 1–12 from top to bottom. A different gesso fill was poured into each mortise, allowed to dry for 5 days and sanded to a uniform thickness using a jig. All of the test materials were formulated with 100g pigment in 50 ml of rabbit skin glue. The materials used to make the gesso fills are listed in Table 1.

Each panel was examined by x-radiography with a Picker SN262 x-ray instrument for 60 seconds at 23.5 kV x 5 mA x 60 seconds. Kodak Industrex MX-125 x-ray film was used and developed at the maximum development time (Kodak manual developer).

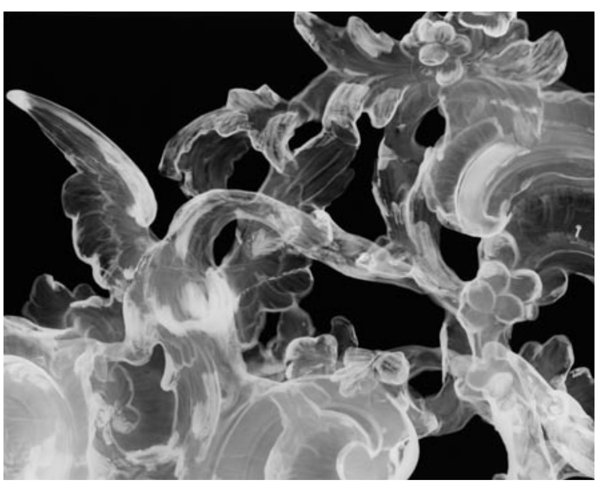

Figure 4. In this x-radiograph taken after the gesso fills the areas of fill are clearly visible.

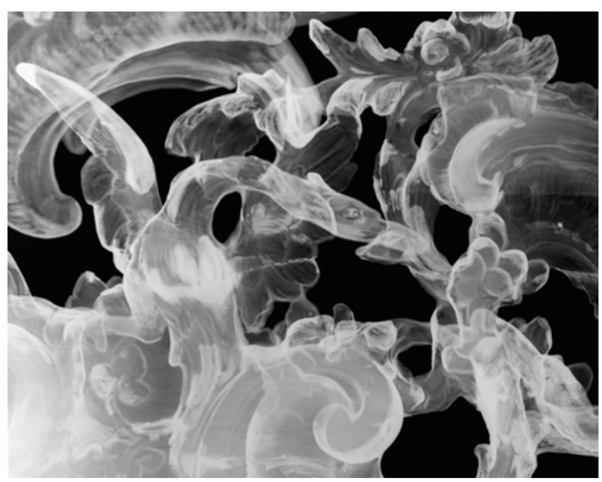

Figure 5. This x-radiograph was taken after bole and gold leaf have been applied to the areas of loss. There is no perceptible difference between this x-radiograph and the one with only gesso in figure 4.

Results and Discussion

Test Panel #1

The first test panel compared the x-ray densities of several traditional gesso materials without added pigments (mortises 3-10). This panel also tested the two different forms of barium sulfate when added to calcium carbonate against the two highest concentrations of bismuth oxide used in the previous tests. Test panel #1 contained the formulations shown in Table 2.

The x-radiography image of this panel is shown in figure 6. Considerable cracking was observed when 20% precipitated barium sulfate was formulated with calcium carbonate (mortise 1), a result consistent with our 2002 observations. Interestingly, the same concentration of blanc fixe, which is a mined barium sulfate, caused much less cracking as seen in mortise 12. However, the two forms of barium sulfate had similar small effects on the x-ray density of the gesso when compared to the bismuth oxide samples shown in mortises 2 and 11.

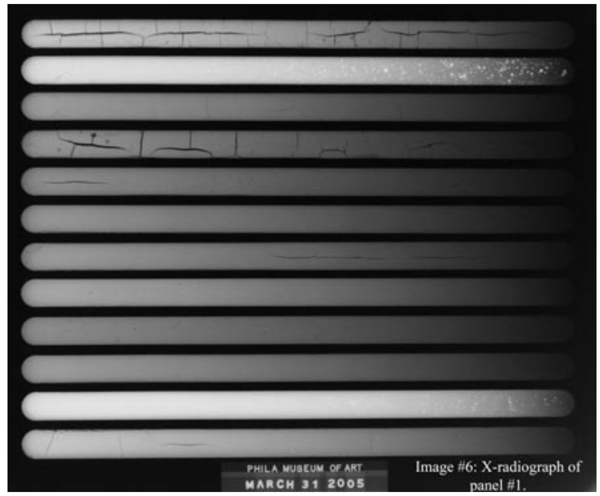

Figure 6. Test panel #1.

Mortises 3-10 show that the traditional gesso fill materials have very slight but perceptible differences in x-ray density. The differences are clearly not great enough to discriminate them as fills without added x-ray dense pigment. Of these gessoes, the anhydrite plaster in mortise 8 exhibited the greatest x-ray density, and therefore was used as a control in the development of the bismuth

Table 1. Materials used to make gesso fills.

Common Name	Chemical Name	Chemical Formula
Alabaster plaster	Anhydrite	$CaSO_4$
Anhydrite plaster	Anhydrite	$CaSO_4$
Barium sulfate	Barium sulfate*	$BaSO_4$
Bismuth oxide	Bismuth oxide*	Bi_2O_3
Blanc fixe	Barium sulfate, mined	$BaSO_4$
Bologna chalk	Calcium carbonate + Calcium sulfate dihydrate	$CaCO_3 + CaSO_4{\cdot}2H_2O$
Calcium carbonate	Calcium carbonate + calcium magnesium carbonate	$CaCO_3 + CaMg(CO_3)_2$
Calcium sulfate	Anhydrite*	$CaSO_4$
Chalk from Champagne, France	Calcium carbonate + Silicon dioxide	$CaCO_3 + SiO_2$
English China clay	Aluminum hydroxide silicate	$Al_2(OH)_4Si_2O_5$
Marble dust, extra fine grind	Calcium carbonate	$CaCO_3$
Sarti chalk	Calcium carbonate + anhydrite	$CaCO_3 + CaSO_4$
Terra alba gypsum	Calcium sulfate dehydrate + Anhydrite	$CaSO_4{\cdot}2H_2O + CaSO_4$

Table 2. Test Panel #1 Gesso Formulations in 50mL Rabbit Skin Glue

Mortise #	Filler (# of Grams)	Pigment (# of Grams)
1	Calcium carbonate (80 g)	Precipitated barium sulfate (20 g)
2	Calcium carbonate (85 g)	Bismuth oxide (15 g)
3	Sarti Chalk (100 g)	-
4	Alabaster plaster (100 g)	-
5	Terra alba gypsum (100 g)	-
6	Calcium carbonate (100 g)	-
7	Bologna chalk (100 g)	-
8	Anhydrite plaster (100 g)	-
9	Calcium sulfate (100 g)	-
10	Marble dust, extra fine grind (100 g)	-
11	Calcium carbonate (80 g)	Bismuth oxide (20 g)
12	Calcium carbonate (80 g)	Blanc fixe [mined barium sulfate] (20 g)

oxide-modified gessoes.

Test Panel #2

The second panel (Table 3) shows the effects of different concentrations of bismuth oxide in a calcium carbonate gesso (5-20% by weight based on the weight of the pigment plus carbonate). It also tested x-ray density of the Champagne chalk (a late arriver which did not make it for panel #1) and the effectiveness of the China clay as a gesso material alone as well as a fill material with anhydrite plaster. The x-radiography image of this panel is shown in fig. 7.

The x-ray density of the Champagne chalk (mortise #1) is similar to other chalks tested. The China clay did not perform well as a gesso material alone, as evidenced by the complete loss of fill in mortise 2, nor did it perform well as a filler, as evidenced by the cracks visible in mortise 3.

Figure 7. Test panel #2.

As mentioned earlier, 100% anhydrite plaster was the densest gesso material from Test Panel 1 and, as such, served as the control in alternating mortises. Though x-ray density increases with as little as 5% bismuth oxide (mortise 5), the differences become much more pronounced as the bismuth oxide concentrations are increased from 10 to 20% (mortises 7, 9 and 11). Gessoes modified with a higher level of bismuth oxide appear to be useful for discriminating these fills from original gessoes while maintaining optimal working properties.

The x-ray density of the bismuth oxide-modified gesso at 5% is perceptibly different from the control anhydrite plaster along 95% of the length of the mortises, which range from 1/16″ to ¼″ thick. However, at 10% concentration of bismuth oxide, the fill can be discriminated from the control along 100% of the length of the mortise, although weakly at the thin end. At 15% the difference becomes more pronounced, and at 20% concentration the fill can be discriminated quite easily along 100% of the length of mortise.

Conclusion

Barium sulfate in its precipitated form had failed

Table 3. Test Panel #2 Gesso Formulations in 50 mL Rabbit Skin Glue

Mortise #	Filler (# of grams)	Pigment (# of grams)
1	Chalk From Champagne France (100 g)	-
2	English China Clay (100 g)	-
3	Anhydrite Plaster (50 g)	English China Clay (50 g)
4	Anhydrite Plaster (100 g)	-
5	Calcium carbonate (95 g)	Bismuth Oxide (5 g)
6	Anhydrite Plaster (100 g)	-
7	Calcium Carbonate (90 g)	Bismuth Oxide (10 g)
8	Anhydrite Plaster (100 g)	-
9	Calcium Carbonate (85 g)	Bismuth Oxide (15 g)
10	Anhydrite Plaster (100 g)	-
11	Calcium carbonate (80 g)	Bismuth oxide (20 g)
12	Anhydrite Plaster (100 g)	Blank fixe (20 g)

in our earlier studies. We found that the use of a different form of barium sulfate—blanc fixe—improved the working properties of the material. However, its effect on x-ray density was inferior to bismuth oxide.

We also had reported earlier that when bismuth oxide and zinc oxide were both added to a calcium carbonate gesso in rabbit skin glue, the modified gesso was easy to distinguish from original gesso by x-radiography. We have now expanded our study to a number of traditional gesso materials, which turn out to have similar x-ray densities, with anhydrite plaster being slightly denser.

We were able to modify a calcium carbonate gesso by adding bismuth oxide pigment at various concentrations ranging from 5 to 20%. At these concentrations, the modified gesso could be distinguished readily from anhydrite plaster, except when the application was very thin (under about 1/8″). The addition of the bismuth oxide did not alter the working properties of the material. Notably, we were able to achieve this greater x-ray density without the zinc oxide used in our 2002 research, which had a whitening effect on the gesso and may be undesirable for some objects.

English China clay was found to be a poor performer, both as a substitute for the more traditional gesso materials and as an additive.

Future studies could include assessment of long-term stability of the formulated fill materials.

Acknowledgements

I would like to thank David deMuzio for his input in design and implementation of this study; Andrew Lins, Beth Price, and Ken Sutherland for analysis of the materials used; and Joe Mikuliak for x-radiography and photography.

Endnotes

1 The compositions of these materials were verified by using Fourier transform infrared spectroscopy and x-ray diffraction analyses, which were performed by Andrew Lins, Beth Price, and Ken Sutherland. The instrumental conditions, sample preparation information, and data are on file at the PMA and are available upon request.

2 The stock solution of rabbit skin glue was made by dissolving 45 grams of ground rabbit skin glue in 1000 ml of distilled water.

3 The suppliers for test materials were: Kremer Pigments, Fischer Chemical Products, Fluka Chemical Corp, Sepp Leaf Products, and Del-Val Pottery Supply.