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STORAGE OF ARCHAEOLOGICAL TEXTILE FINDS IN SEALED BOXES

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Abstract—A white deposit was observed on the glass lids of boxes used to store archaeological textile fragments for some 40 years. It was identified as sodium formate formed from formaldehyde given off by cardboard in the boxes. Heavy metal ions in some samples of the deposit originated, via the textile fragments, from corroded bronze ornaments in the graves.

1. INTRODUCTION

In comparison with other materials, textiles are rarely found in archaeological investigations, a fact which makes their conservation particularly important. The rich complex of textile finds of the ninth—tenth century from Birka in Lake Mälaren, Sweden, is one of the best known, not only for its intrinsic interest but also on account of its treatment and the publication of Agnes Geijer [1].

From the time of the excavations at Birka in 1871–81 up till the 1930s the textiles were left untreated. In the 1930s the work of separating the textile fragments from their earth and clay covering started, while methods were developed for their treatment. Cleaning was carried out with distilled water.

Mounting of the textiles was carried out so as to afford both protection and easy access for research. Two types of mounting were used: between glass plates, and in cardboard boxes covered by glass. With the double glass mounting, the glasses were kept apart with paper spacers and held together with adhesive plaster. The fragments were sometimes held in place with a drop of adhesive or, when they consisted of partly loose threads, were placed on 'crepelin', a fine silk veil. With the boxes, a piece of cardboard covered in rough silk shantung was placed in the bottom of the box and the fragments either rested loosely on this or were held in place by a thin silk thread stretched over them.

With few exceptions the boxes remained sealed until 1975. The fragile material has stood up well thanks to the protection from direct handling. In 1975, however, a white coating was observed on the inside of the glass of the boxes. An investigation was undertaken to find out if this was harmful to the textiles and what its origins were.

2. IDENTIFICATION OF THE WHITE COATING

At an early stage of the investigation a mass spectrometric analysis of the white deposit was made. Of the 14 elements detected, sodium was the main component but there was also a remarkably high lead content. This last was surprising and needed explaining. A search for its origins was therefore made later though in the end it proved to be irrelevant to the main question of the white deposit.

Under the microscope (magnification $\times 100$) two types of particles could be seen: droplets and prisms (Fig. 1). The photographs were taken through the glass before opening the boxes. A small amount of the crystalline material was scraped from the glass and examined by X-ray diffraction [2]. The resulting diffraction pattern was compared, using a computer data-processor, with a reference library of diffraction patterns stored on magnetic tape [3]. It proved to be that of the small and simple molecule sodium formate, $HCOONa$.

X-ray diffraction does not give useful results with amorphous materials and therefore

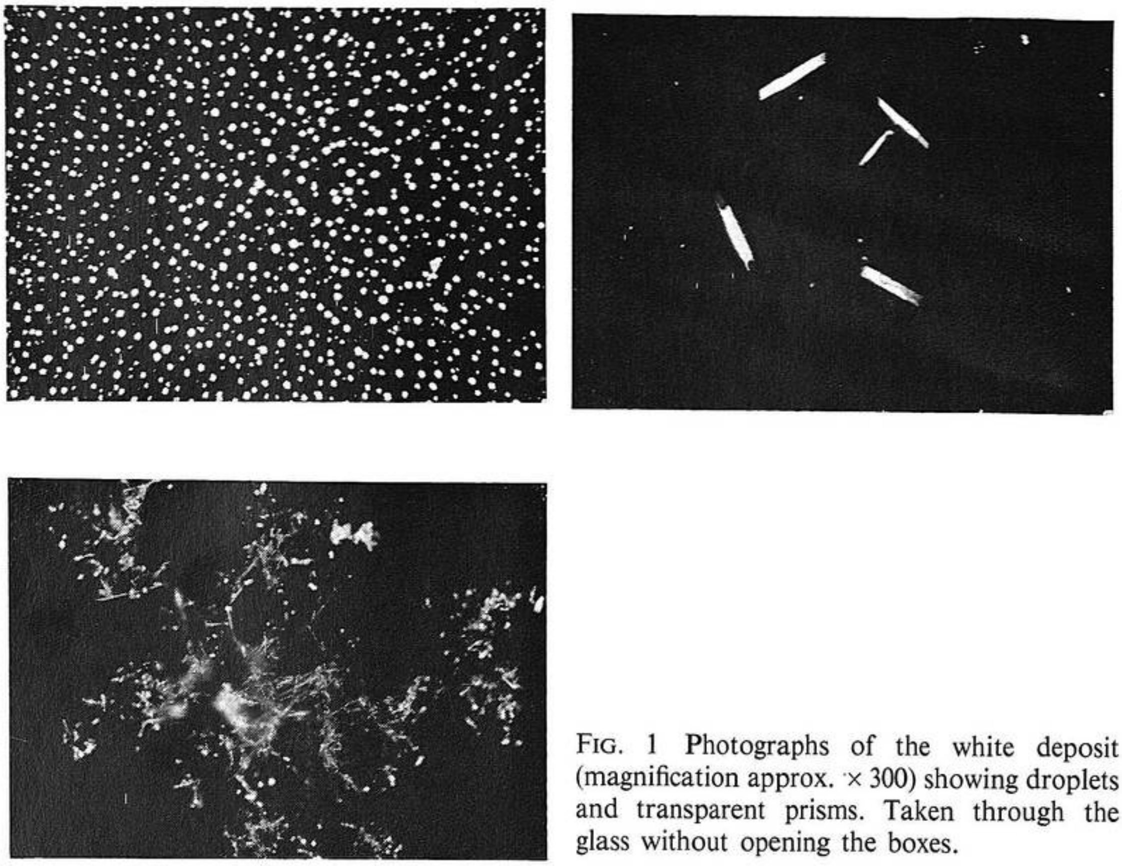

FIG. 1 Photographs of the white deposit (magnification approx. × 300) showing droplets and transparent prisms. Taken through the glass without opening the boxes.

could not be used for the droplets. Infrared spectroscopy, however, showed the crystalline and amorphous materials to be the same chemically, and confirmed their identification as sodium formate.

3. ORIGIN OF THE HEAVY METALS

To try and determine the origin of the lead in the first sample of the white deposit examined, different items were analysed by X-ray fluorescence spectroscopy [4] which is non-destructive and shows up the presence of aluminium and all heavier elements. The instrument used was a Phillips type PW 1540 equipped with LiF and ADP crystals. The results are summarized in Table 1.

The heavy elements clearly originate mainly from the bronze objects occurring alongside the textiles in the graves. The lead has been localized to the ornaments where it has been used in the knobs of oval brooches [5]. Iron occurs as separate parts of these ornaments, e.g. the pins on the back. It is interesting to note that, with few exceptions, woollen cloth is only found close to metal parts. The most likely explanation for this is that most soil fungi and other organisms have been killed by the metal ions, especially by the copper.

It will be noticed that in Table 1 the sample of white coating examined showed no heavy elements. The explanation for the different findings proved to be that in some cases the boxes had been stored inverted and the textile fragments had been in contact with the glass. Only in these cases had heavy elements been transferred to the coating.

4. ORIGIN OF THE WHITE COATING

The white coating occurs in all the sealed boxes. The explanation of its origin therefore has probably been provided by the photography scientist Runo Kohlbeck [6] who claims that

TABLE 1

Item	*X-ray analysis (metal distribution)*
1 Adhesive plaster (from 1930)	No heavy elements
2 Paper strips, 1 × 5 mm, for spacing the glass plates	No heavy elements
3 Glass plate	No heavy elements
4 Horse skeleton + soil	Small amount of iron
5 Female skeleton	Copper : zinc : iron 10 : 3 : 1
6 Bronze ornament (fragment)	Copper : iron with lead and zinc 10 : 3 (small amounts)
7 Bronze ornament (fragment)	Copper : iron with lead and zinc 10 : 3 (small amounts)
8 Woollen cloth	Copper and lead. Small amounts of zinc and iron
9 White coating	No heavy elements

all paper qualities, with the possible exception of rag paper, give off small quantities of formaldehyde which can autoxidize in time to formic acid. The effects of this will naturally be more noticeable in a sealed container as here. The formic acid must have reacted with sodium compounds in the glass to give the sodium formate.

There was no evidence for any fungal or bacterial activity in the boxes which is understandable since formaldehyde has good fungicidal and bactericidal properties. The presence of cheap paper is therefore an excellent preservative agent from this point of view when used in sealed boxes. At the same time the formation of formic acid itself would seem to be undesirable and a threat to the survival of organic materials, as in fact in the case of paper itself where de-acidification may become necessary [7, 8].

The above findings serve to show up the unanticipated effects of materials over long periods of time and emphasize the need for further research to solve the problems of long-term storage of unique finds.

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Abstrait—Les couvercles de verre de boîtes dans lesquelles furent conservés pendant près de quarante ans des spécimens de textile en provenance de fouilles archéologiques présentaient un dépôt blanc. Ce dépôt se révèla à l'analyse être du formiate de sodium, provenant de formaldéhyde dégagé par le carton des boîtes. Les ions de métaux lourds présents dans certains échantillons du dépôt provenaient de parures en bronze corrodé trouvées dans les tombes en même temps que les fragments de textile.

Kurzfassung—Auf den Glasdeckeln von Kästen, die seit einigen 40 Jahren für die Aufbewahrung von archäologischen Textilfragmenten dienten, wurde eine weiße Ablagerung beobachtet. Sie konnte als ameisensaures Natrium (Natriumformiat) bestimmt werden, das sich aus dem von der Pappe in den Kästen abgegebenen Formaldehyd bildete. Schwermetallionen in einigen Proben der Ablagerung entstanden—über die Textilfragmente—aus korrodierten Bronzeornamenten in den Gräbern.