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# Exploring photozincographic metal plates collections: Manufacturing techniques and zinc corrosion

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## Abstract

This study explores the materials, manufacturing processes, and corrosion behavior of photozincographic plates from the Lactário Museum in Lisbon, Portugal. Analysis of thirty-three historical plates (1927–1971) and three non-historical plates using stereomicroscopy, micro-X-ray fluorescence, X-ray diffraction, and accelerated aging tests revealed that the plates are primarily composed of zinc with trace elements (lead, iron, and calcium) and produced by distinct manufacturing techniques. Corrosion products containing sulfur-based compounds indicate

the influence of an outdoor environment. Accelerated aging demonstrates significant image degradation from corrosion, highlighting the need for tailored preservation strategies for these unique composite objects.

## Keywords

photozincography, photomechanical process, zinc corrosion

## Introduction

Photozincography, a 19th century photomechanical process, involves transferring photographic images onto zinc plates for printing (James 1860). While paper prints have been well-studied (Stulik and Kaplan 2013), zinc plates remain underexplored despite their historical and technical importance. These plates provide insights into early photomechanical processes and production records but limited understanding of their manufacturing techniques and corrosion mechanisms leads to data loss and challenges in conserving them. Key questions persist regarding variations in manufacturing techniques, the impact of fabrication on degradation, primary causes of corrosion, and effective mitigation strategies. This study seeks to address these gaps by analyzing the materials, manufacturing techniques, and influence of environmental conditions and composition on zinc plate corrosion.

A comprehensive investigation of photozincographic plates from the Lactário Museum in Lisbon, Portugal, examined these 20th century objects as models for the evolution of manufacturing techniques. Recent severe atmospheric

corrosion of many plates, characterized by white or grey adherent products, underscores the urgent need for effective conservation and preservation methods.

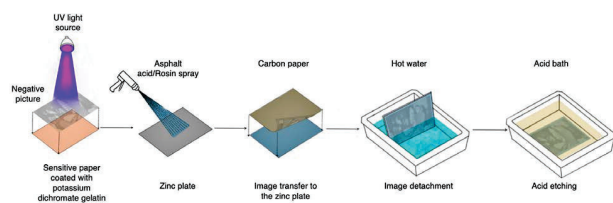
## Photozincography—Photomechanical process for printing

In the photozincographic process, a zinc plate was polished using a damp cloth dipped in levigated pumice powder to create a smooth surface (Waterhouse 1890). A light-sensitive paper coated with a potassium dichromate gelatin layer was exposed to light under a photographic negative. During exposure, the gelatin hardened due to cross-linking, rendering it insoluble (Hanson 2017).

The zinc plate was sprayed with asphalt acid or rosin for image transfer. The prepared image was transferred to the plate, which was then immersed in hot water to detach the gelatin layer from the paper. After drying, the plate was pickled in solutions such as nitric acid, hydrochloric acid or copper sulfate. The hardened gelatin layer protected

the plate during acid etching, creating a textured surface with cell-like structures necessary for ink retention in printing (Wilkinson 1886).

Various inks could be applied for the printing process, including formulations combining chromium salts with animal glue (Waterhouse 1890). The photomechanical process is illustrated in Figure 1.



**Figure 1** Manufacturing process of photozincographic metal plates

### The collection of photozincographic plates from the Lactário Museum

The Lactário Museum's collection showcases the *Associação Protectora da Primeira Infância's* (APPI) contributions to early 20th century pediatric care and public health in Lisbon, including support for needy families and children. The collection comprises objects related to science, technology, art, and social services, such as Portugal's first baby incubators (Cavadas de Oliveira and Tissot 2019). Around 140 photozincographic plates have been preserved, documenting APPI activities, the development of social and health services in Portugal, and the work of various photographers and studios, illustrating the evolution of photozincography as a photomechanical image reproduction technique.

### Methodology

The study was divided into two parts: i) characterization of materials and manufacturing techniques and ii) corrosion study. The corpus included 33 plates from the Lactário Museum (1927–1971) arranged chronologically and by negative provenance, and three non-historical plates for comparison.

Elemental composition was analyzed using a Bruker M4  $\mu$ X-ray fluorescence (XRF) spectrometer with a Rh target X-ray tube, XFlash SDD detector, with a 25  $\mu$ m spot size. Measurements were performed at 50 kV and 300  $\mu$ A for 120 s. Manufacturing techniques were examined using a Leica M205C stereomicroscope at various magnifications.

The influence of materials on plate corrosion, especially acids from wooden blocks and paper enclosures, was tested using bromocresol green dye-coated paper strips (A-D strips). A severely corroded photozincography plate from the museum was sealed with the strips and paper in an aluminized polyethylene barrier (Marvelseal® 360) to monitor acetic acid release (Nicholson and O'Loughlin 1996).

Corrosion morphology and products were studied using visual inspection, stereomicroscopy, XRF for elemental composition, and X-ray diffraction (XRD) for identification of crystalline phases using a Bruker D8 Advance with Cu K $\alpha$  radiation. Data was collected with a 0.015° step size and a 0.2 s/step acquisition time.

Accelerated aging of non-historical plates, was conducted using a neutral salt spray in an ERICHSEN 606/400L climate chamber following ISO 9227:2022. Plates were positioned at 45° and horizontally. Corrosion products were analyzed following the same protocol used for the historical plates.

## Results and discussion

### Materials and manufacturing techniques

Photozincographic objects consist of a zinc plate mounted on a wooden block, secured with nails, and enclosed in a sealed paper cover with an attached photomechanical print (Figure 2). Plate sizes ranged from 6.5 to 13 cm in height and from 9 to 18 cm in width.

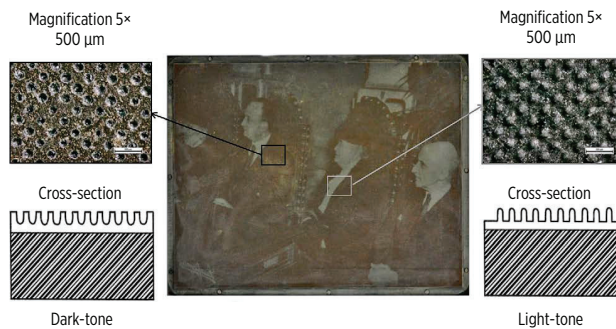


**Figure 2** Photozincographic object from the Lactário Museum: paper cover and cross section photo of the plate

The earlier plates had a darker surface, whereas the latter exhibited a yellowish hue. XRF analysis detected higher chromium levels in the yellowish plates, likely due to chromium-based inks (Waterhouse 1890). The darker appearance of the earlier plates may be due to different ink formulations, although not identifiable by XRF.

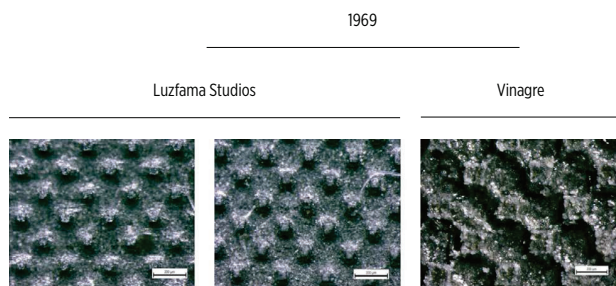
The collection includes halftone photozincographic plates with distinct matrix patterns. Stereomicroscopic analysis identified two main planes (Figure 3):

- Dark-tone plane (highest): associated with black shades, displaying circular cell patterns.
- Light-tone plane (lowest): linked to the white or light grey shades, featuring cylindrical or cubic rises.



**Figure 3** Photozincographic plate from the museum with microscopic images and cross-section schemes of the dark-tone and light-tone matrix planes

Observations also highlighted variability across plates, even from the same year, which could be related to studios or production techniques. For instance, two plates from 1969 by the Luzfama studio shared identical light-tone patterns, whereas another 1969 plate by Vinagre displayed distinct cubic patterns (Figure 4). These differences suggest that the methods used to capture negatives (such as the specific cameras and techniques, or the use of a fine fabric placed between camera lenses to create grain) significantly influenced the zinc matrix patterns (Wilkinson 1886).



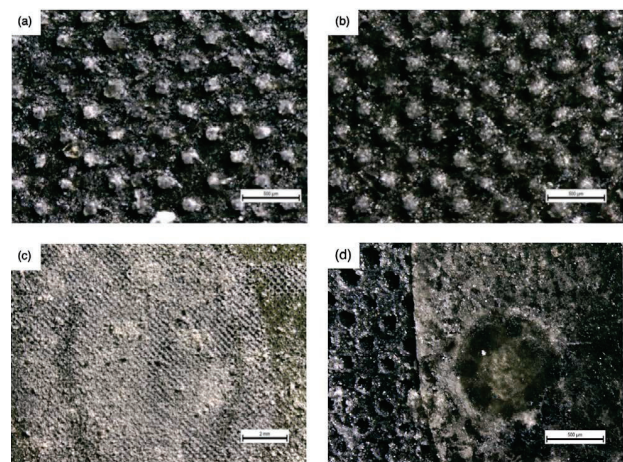
**Figure 4** Microscopic images of the light-tone plane of three plates dated 1969, made after negatives with different authorship

This pattern variability suggests that photozincographic plates can potentially be attributed to specific studios or photographers through matrix shape analysis. However, expanding the study corpus is necessary to establish reliable dating methods.

Elemental analysis showed that the plates were primarily zinc (98 percent), with traces of lead, iron, and calcium. Calcium impurities likely come from the zinc oxide ore used, which was chosen over zinc sulfide ores to reduce sulfur emissions (Soltani et al. 2021). No significant differences in elemental composition were found across the plates, except for higher chromium levels in the yellowish plates, which were attributed to the ink.

### Corrosion study

Stereomicroscopy revealed various corrosion morphologies on museum plates, including uniform crystalline corrosion, yellow to brown compounds on chromium-based ink plates, and bulkier corrosion around frames (Figure 5). One plate displayed small platelet islands, characteristic of marine corrosion, likely caused by chlorine-based products (Zhang 1996).



**Figure 5** Microscopic images of corrosion products from Lactário Museum plates: (a) uniform white corrosion layer; (b) uniform transparent corrosion layer; (c) localized bulky white corrosion; (d) localized platelet island corrosion

XRF analysis detected sulfur in all the plates. By XRD, zinc oxide (zincite) and zinc sulphate (boyleite) were identified. However, the presence of zinc chlorides in trace amounts cannot be excluded. The possible presence of chlorine compounds in trace amounts could result from the degradation of certain wood types or from outdoor atmospheric influences, with its detection limit by XRF falling below the threshold. The presence of sulfur points to corrosion influenced by the external environment (Christopher et al. 2016). Given the museum's proximity to the Tagus River and Lisbon's yacht quay, sulfate and chloride compounds are likely the primary pollutants (Figure 6).

A-D strips showed darker blue-to-green shifts for plywood, indicating higher acid release compared to paper (Figure 7).



Figure 6 Map with the position of Lactário Museum

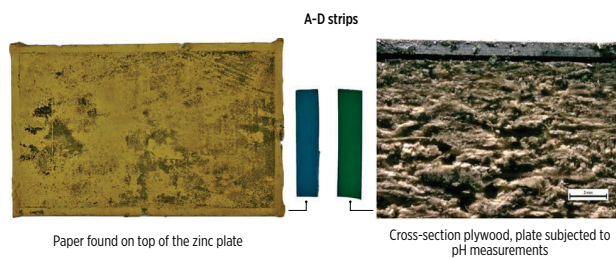


Figure 7 A-D strips results after 2 weeks

Although specific acids remain unidentified, they can accelerate zinc corrosion upon contact (Zhang 1996).

To simulate museum conditions in environments with maritime influence and assess image loss, two non-historical plates underwent accelerated aging with humidity cycling and neutral salt spraying (Figure 8). After 45 h of continuous salt spraying, both plates showed significant degradation, and were fully covered in corrosion products.

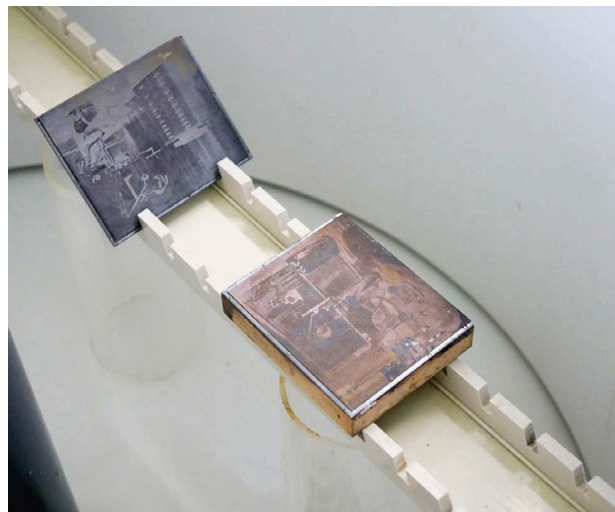


Figure 8 Chamber picture before accelerated artificial aging process on two non-historical plates

The artificially aged plates displayed corrosion products similar to those on museum plates, along with chloride-based corrosion products. These included heterogeneous, layered island platelets in various colours and sizes (Figure 9).

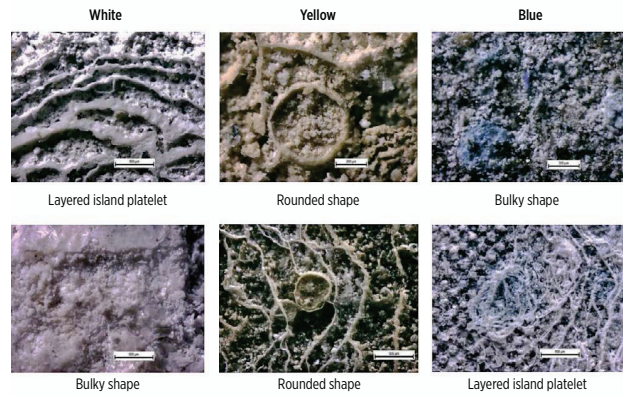


Figure 9 Microscopic images of the corrosion products and their morphology, found on artificially aged plates

The corrosion colours align with documented zinc oxides, hydroxides, and simonkolleite (Lage de la Rosa 2006). The corrosion was thicker and highly crystalline owing to the aggressive environment, with XRD analysis detecting simonkolleite and zinc hydroxide dihydrate ( $Zn(OH)_2$ ). Crystalline corrosion suggests accelerated deterioration owing to marine influences (De la Fuente et al. 2007). The museum plate displayed a more complex corrosion profile, indicating an exposure to various environments. Analyzing the accelerated aging tests was essential for understanding degradation and information loss. Partial cleaning of an aged plate (Figure 10a) with a five percent EDTA solution revealed significant pitting corrosion (Figure 10b) and detachment of historical materials, such as ink (Figure 10c), highlighting the vulnerability of photozincographic collections to atmospheric corrosion-induced information loss.

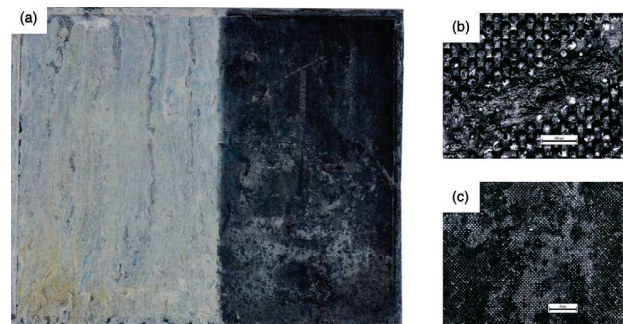


Figure 10 Assessing loss of information: (a) half cleaned non-historical plate after artificial aging; (b) pitting corrosion; (c) ink detachment

## Conclusion

Manufacturing variances in photomechanical plates were examined, with matrix pattern differences attributed to studios or photographers reflecting their equipment and techniques. Although no chronological distinctions were found, plates from the same studio exhibited similar light-tone patterns, suggesting that the camera and lenses influenced matrix structure.

Corrosion products containing sulfur and likely chloride-based compounds result from outdoor environmental factors particularly from the museum's simultaneously coastal and urban location. Morphologies included crystal-line deposits, bulkier corrosion, and small platelet islands. Similar corrosion patterns found on both museum and artificially aged plates emphasize the role of coastal aerosols in accelerating degradation. Chlorine and sulfur contents may also come from certain wood degradation, warranting further research. Additionally, Acid Detection (AD) indicators confirmed that the release of acids from wood and paper materials is a contributing factor to corrosion.

The study highlighted the risks of image loss due to pitting corrosion and ink degradation, necessitating the reconsideration of conservation methods for exhibiting and storing these collections. To our knowledge, this is a pivotal work that highlights the risk of loss of such objects. The results support the development of preventive and curatorial conservation strategies and display options for metal plate collections used in photomechanical print production.

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