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Photograph: Detail from 'Bridge No. 2' from the series *Rust Never Sleeps*, John Moore, 1996

CONSERVATION OF PIGEON CAMERAS: A COLLABORATIVE APPROACH BETWEEN CONSERVATORS AND SCIENTISTS

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Abstract

This paper presents findings from the examination and technical analysis of three small pigeon cameras from the 1930's belonging to the Swiss Camera Museum in Vevey, Switzerland. The analysis was undertaken in 2006 in preparation for a new exhibition 'des pigeons photographes' at the Museum. The small cameras were designed for attachment to the underbelly of carrier pigeons to obtain aerial photographs for military use. The components of the camera are very small and consist of different metal alloys, paint, textile and glass. Some of the components were covered by a thick layer of white corrosion products. Compositional information was obtained using energy dispersive X-ray spectroscopy (EDS). The corrosion products were analyzed with micro X-ray fluorescence (XRF), micro Raman spectroscopy and micro Fourier transformation infrared (FTIR) spectroscopy. Results indicate that the alloys used in the manufacture of the camera are aluminium/magnesium, magnesium/zinc and copper/zinc alloys. The white corrosion products were found to be a mixture of magnesium acetate and magnesium carbonate hydroxide hydrate. Results also establish the presence of cellulose acetate, the likely cause of the corrosion.

Keywords: magnesium acetate, magnesium carbonate hydroxide hydrate, XRF, Raman, FTIR, XRD, aluminium alloy, magnesium/aluminium alloy.

Introduction

In 1908, aerial photographs of a castle in Bavaria, Germany, were taken by a camera developed for carrier pigeons by Julius Neubronner. However, Neubronner's invention was not made public at that time. More than 20 years later in Switzerland, Christian Adrian Michel, the head of a family business of watchmakers in Walde, Switzerland, heard about this idea, refined it and developed the first prototype camera intended for commercial production (see Figure 1). He adapted the camera to 16 mm films and without increasing the weight of the camera he introduced a miniaturised timer, which controlled the start delay as well as the time between the exposures.

After he applied for a patent, Michel proposed the use of the pigeon cameras to the Swiss army in 1937. In the same year, the first tests were carried out on aircraft at the Dübendorf (Zürich) airport. Further tests using different cameras carried by pigeons resulted in eight films of good quality. After writing a manual for the use of the camera, Michel approached various companies that could manufacture it. The outbreak out of World

War II in 1939 ended the project and the pigeon cameras were never commercialised. In 2004, Michel's children donated the cameras, manuals, films and associated documents to the Swiss Camera Museum in Vevey, Switzerland (Bonnard Yersin and Bonnard Yersin 2007).

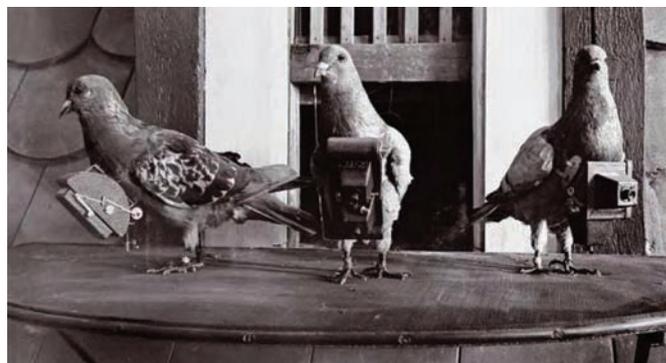


Figure 1. Historical photograph showing how the cameras were attached to the pigeon.

For decades, the cameras were stored in uncontrolled conditions in Michel's factory. By 2006, the collection

was in a poor state of preservation and the Museum of Vevey sent a set of camera parts to Art Metal Conservation GmbH (AMC), a private conservation firm in Basel, Switzerland, for conservation treatment.

The complexity involved in treatment of these composite objects made a preliminary study of the cameras' materials a necessity. In order to choose the best strategies for restoration and preventive conservation, AMC approached the scientists at the Laboratory of Conservation Research (LCR) and the Laboratory of Inorganic Chemistry (LCI) at the Swiss Federal Institute of Technology in Zürich to assist with this project and to provide answers to several questions: Why were some parts of the cameras heavily corroded and others not? What were the corrosion products? Which of the materials contributed to the corrosion and what was causing it?

The pigeon camera collection

The collection of objects that were donated to the museum comprised three cameras and numerous spare parts. A visual study of these parts provided an understanding of the cameras and how to dismantle them. Examination also provided information about manufacture of the camera parts and their attachment to the camera body by methods such as welding, crimping, riveting, bolting with miniature screws and interlocking (see Figure 2 and 3).



Figure 2. Two examples of pigeon cameras.



Figure 3. The components of the release mechanism.

In comparison with common commercial cameras, the components of the pigeon cameras are like miniatures (see Figure 4; all parts of the camera referred to below are shown and numbered in Figure 4). To save weight, most of them contain holes or are made of lightweight materials. The cameras are complex devices with a small inner chamber that consists of a bottom part and an upper part made from two different, bright metal alloys (see Figure 4, number 1 is the lower part and number 2 is the upper part). The inner chamber contains the film reel that is painted black (number 3 in Figure 4), the film roll (number 4 in Figure 4), including the film itself (number 5 in Figure 4) and a reel cap (number 6 in Figure 4). The film roll and reel cap are made from a shiny, golden colored metal alloy. The interior of the inner chamber that contains the film reel is painted black, and has an opening for the attachment of an objective with lens (number 7 and 8 in Figure 4). The chamber is sealed with black textile (number 9 in Figure 4) against light. It fits into a casing that is also painted black (number 10 in Figure 4) and contains the automatic release mechanism (number 11 in Figure 4). These parts were partially dismantled for conservation.

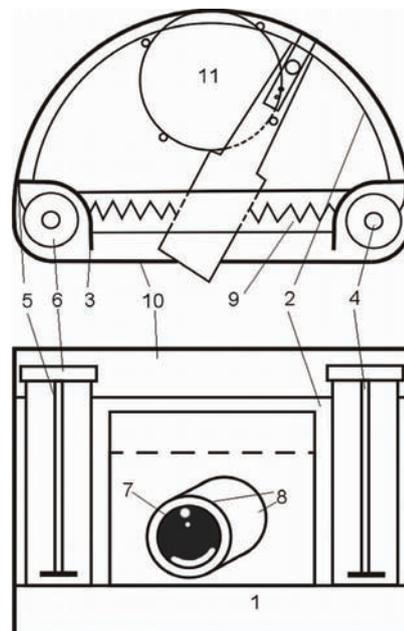


Figure 4. Schematic drawing of a pigeon camera; part numbers are referenced in the text.



Figure 5. A pigeon camera, corroded objective and film reel before treatment. A thick white layer of corrosion is visible.

State of preservation and diagnosis

When examined, many of the cameras' parts appeared to be actively corroding with the corrosion spread over the entire camera (see Figure 5 and 8). A strikingly thick layer of white corrosion products were visible underneath the black paint and covered both the metal surface and the other materials associated with it. Another type of efflorescence consisting of light, microcrystalline powder seemed to affect only certain grey metal parts. A closer look revealed that these white corrosion products appeared only on components that were connected to other parts that appeared to be shiny and uncorroded.

Underneath the corrosion products, the metal surface was no longer smooth but appeared grainy and grey in color. It was obvious that one or more specific kinds of corrosion were occurring on the metal surfaces, a result of different metal alloys used in the construction of the camera. The corrosion affected only certain components of the cameras, such as the outer part of the lens ring, the tubes containing the film and the lids of the tubes. Some components were deeply corroded and others, such as the camera body and inner part of the objective, were immaculate.

Developing a treatment strategy

A close collaboration between scientists and conservators was essential in order to choose the best strategy for restoration and preventive conservation. It was crucial to find the possible causes and processes responsible for the corrosion and to characterise the corrosion products. Despite the fact that the cameras' parts are made from several different metals, there was no evidence of galvanic or pitting corrosion.

Given that identification of the type or types of corrosion visible on the various camera components would be the basis for devising a treatment plan, analysis began with the identification of the different white corrosion products. The next step was to determine why certain components of metal were corroding, while others appeared to be free of corrosion.

Methodology, results and discussion

The LCR works in close collaboration with curators and conservators, and specializes in the use of analytical technologies for the examination, characterisation and analysis of objects of cultural and historical interest, and conducts research on cultural heritage and historical materials. The LCR analysed the alloys and corrosion products from various camera parts using micro X-ray fluorescence (XRF), micro Raman, and micro Fourier transform infrared (FTIR). LIC carried out X-ray diffraction to characterize the corrosion products.

Metal alloys

The metal alloys of the different parts of the cameras were characterised by using an energy dispersive X-Ray fluorescence spectrometer Eagle III (EDAX, X-ray tube: rhodium target). This is a multi-elemental method (accuracy of the instrument is 0.01 % to 0.05 %) where the measurement accuracy depends upon the different elements and homogeneity of the samples. For elemental analysis, surface areas that are corrosion free are necessary for accuracy. Accordingly, very small areas (approximately 0.5 mm²) were cleaned of corrosion using a scalpel. Approximately 30 areas with a diameter of 50 µm were analysed under the following conditions: Voltage 20 kV, current 100 µA and a dwell time per point of 200s. Because of the inhomogeneity of the alloys themselves, only a semi-quantitative evaluation was possible. Results are listed in Table 1.

| Element | Bottom part of inner section (1) | Upper part of inner section (2) | Film reel (3) | Film roll (4) | Film reel cap (6) | Inner part of the objective (7) | Outer part of the objective (8) |
|---------|----------------------------------|---------------------------------|---------------|---------------|-------------------|---------------------------------|---------------------------------|
| Mg | 0.7 ± 0.1 | 1 ± 0.05 | 92.1 ± 0.2 | 93.2 ± 0.3 | 92.3 ± 0.9 | <LOD | 47.9 ± 0.2 |
| Al | 98.3 ± 0.2 | 94.2 ± 0.3 | 7.1 ± 0.2 | 5.5 ± 0.3 | 5.7 ± 0.4 | <LOD | <0.1 |
| Cu | <0.1 | <0.1 | <0.1 | 0.3 ± 0.05 | 0.4 ± 0.1 | 11 ± 0.5 | <0.1 |
| Zn | <0.1 | <0.1 | <0.1 | <LOD | <LOD | 89 ± 0.5 | 50.9 ± 0.2 |
| Mn | <LOD | 0.8 ± 0.1 | 0.5 ± 0.05 | 0.6 ± 0.1 | 0.7 ± 0.2 | <LOD | <0.1 |
| Si | 0.4 ± 0.1 | 3 ± 0.2 | <LOD | <LOD | <0.1 | <LOD | <LOD |
| Fe | 0.4 ± 0.05 | 0.5 ± 0.1 | <LOD | <LOD | 0.4 ± 0.1 | <LOD | <0.1 |
| Cr | 0.2 ± 0.05 | <0.1 | 0.2 ± 0.05 | <LOD | 0.2 ± 0.1 | <LOD | <LOD |
| Ti | <LOD | 0.3 ± 0.05 | <0.1 | <0.1 | <LOD | <LOD | <LOD |
| Ni | <LOD | <LOD | <0.1 | <0.2 | 0.2 ± 0.05 | <LOD | <0.1 |

Table 1. Semi-quantitative analysis of the composition of the metal from various camera components by means of XRF (w/w %, LOD: limit of detection)

Results indicate that the camera components are made from metals of four different compositions:

The film reels (number 3 in Figure 4), reel caps (number 6 in Figure 4) and film rolls (number 4 in Figure 4): a magnesium/aluminium alloy (Mg 92-93%, Al 5-7%), with traces of Ni, Cu and Fe. The outer part of the objective (number 8 in Figure 4): a zinc/magnesium alloy (Zn 51%, Mg 48%), with traces of Ni, Cu and Fe. The inner part of the objective (number 7 in Figure 4): a zinc/copper alloy (Zn 89%, Cu 11%). The upper and lower part of the body (number 1 and 2 in Figure 4): an aluminium alloy.

The magnesium/aluminium alloy is a relatively modern alloy that is a wrought or cast, lightweight material with a low density. These early magnesium alloys are not very resistant against corrosion because of impurities. Today, it is well known that copper traces, iron and nickel can promote galvanic corrosion of the magnesium matrix. It is now possible to produce very pure magnesium aluminium alloys that are less prone to corrosion (Oettel and Schumann 2005). The high strength-to-weight ratio of magnesium and aluminium base alloys made them attractive for applications such as the pigeon cameras.

Film material, textile and black paint

The examination of the film with a binocular microscope showed that it was made from two layers of different

materials. For the FTIR analysis, a spectrometer Biorad Excalibur FTS 3000 coupled to an Infrared microscope UMA 500, fitted with a mercury cadmium telluride detector was used. Measurements were performed using a micro diamond anvil cell in transmission mode (4000-650 cm^{-1}). It was possible to take small samples (0.2 mm^2) of the carrier material and the surface of the film with a scalpel. The samples were pressed with a diamond cell in order to obtain thin films for the analysis. The spectrum obtained from the carrier material shows the characteristic peak of cellulose acetate, whereas the spectrum obtained from the surface of the film shows peaks that can be attributed to gelatine, normally used as film surface (Neumüller 1985, Socrates 1998, Derrick 1999). A sample of the textile was obtained for analysis using the same method described above. The FTIR spectrum of the textile shows that the main component was cellulose acetate.

The black paint was first analysed using XRF, however, the spectrum obtained did not show relevant functional peaks. The absence of fluorescence peaks indicates that this compound is most likely organic, that is, it may contain only elements with an atomic number smaller than 10. Another sample of the paint was analyzed by FTIR, however the spectrum also did not show relevant functional peaks. A third sample was analyzed by Raman spectroscopy and results showed that the paint was mainly composed of carbon black.

Corrosion products

Compositional analysis revealed that all of the highly corroded components are made of a magnesium/aluminium alloy, with small amounts of aluminium, or of a zinc/magnesium alloy. For the characterisation of the corrosion products by Raman spectroscopy, small samples were removed with a scalpel from the corroded parts of the camera. All Raman spectra were acquired on a LabRam Aramis (Horiba Jobin Yvon) equipped with a Peltier cooled open-electrode CCD (1024x256 pixel), fully automated grating system (600-1800 gr/mm), edge filter and laser selection between a diode laser at 785 nm, a He/Ne laser at 632.8 nm and a Nd:YAG laser at 532 nm. Each corrosion product was pressed on an aluminium plate and positioned on the microscope stage for analysis. Spectra were collected using the 532 nm laser, applying laser power between 0.084 and 0.84 mW (600 gr/mm). Measurement times varied from 100 seconds to 250 seconds. The results indicate that there are two different corrosion products present on the camera (see Figure 6). One is magnesium acetate ($\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4 \text{H}_2\text{O}$), the other a hydrated basic carbonate of magnesium, perhaps hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), dypingite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5\text{H}_2\text{O}$), artinite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), or giorgiosite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5-6\text{H}_2\text{O}$). With Raman analysis it was not possible to distinguish between the different hydrated basic carbonates of magnesium as their spectra are too similar (Canterford 1984, Frost 2008 and Twilley 2006).

For this reason, more specific results were sought by X-ray powder diffraction (Stoe STADIP, $\text{Cu}_K\alpha$ -radiation, Ge-monochromator). The results showed that the thick white corrosion products were the same on all three parts of the camera (see Figure 7). This analysis did not detect magnesium acetate, most likely because of its non-crystallinity, but showed that the main component was in fact giorgiosite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 5-6\text{H}_2\text{O}$).

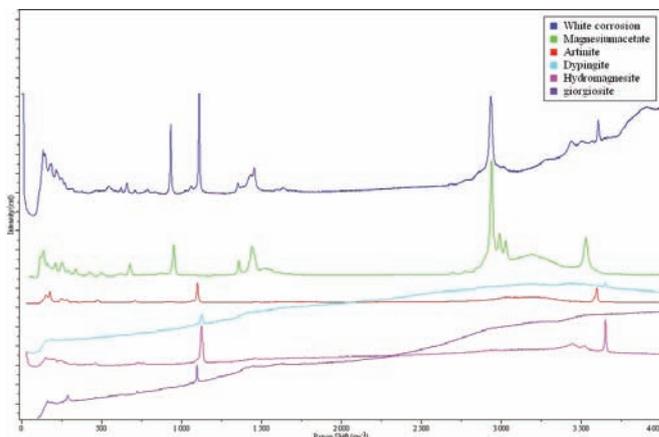


Figure 6. Raman spectra of the corrosion products analyzed from the cameras: unidentified white corrosion products and magnesium acetate were identified in 2006 (dark blue and green spectra), and artinite, dypingite, hydromagnesite and giorgiosite were identified in 2010 (red, light blue, pink and purple spectra), with a shift of circa +10 cm^{-1} due to the aging of the laser.

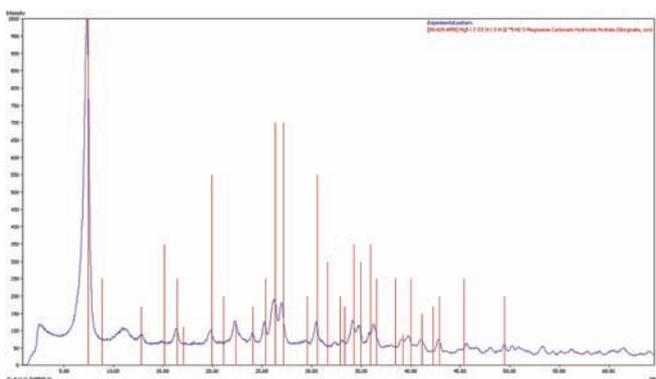


Figure 7. X-ray pattern of the thick white corrosion product, with major phase identification.

Discussion

The most probable reason for the formation of these corrosion products was acetic acid. In this case study, the potential sources of acetic acid are multiple. One possible source could be the cardboard box in which the cameras were stored, which was not acid-free. A second source could be the cellulose acetate contained in the photographic films and the black textile, which forms acetic acid by hydrolysis. This free acid can act like a catalyst for ongoing hydrolysis and reduction of the polymerisation degree. The degradation is promoted by increased relative humidity (RH) (Mills 1994, Waentig 2004).

A complete and detailed reconstruction of the corrosion process is difficult, because on one hand there are

several potential sources of acetic acid (cardboard, films, textiles) and on the other hand, past storage conditions for the objects are not well known and could have changed several times.

Treatment

After determining the potential causes of the corrosion, a conservation strategy was developed. Because these objects were very unusual, no conservation literature about these objects was found. A search of the industrial literature for possible solutions was undertaken, and a decision was made to use a solution of 1g/dm³ of sodium benzoate as a corrosion inhibitor (Rosliza 2007).

After removal of the thickest corrosion layers mechanically, most of the remaining corrosion was removed by means of compresses containing a mixture of ammonium citrate, ethylenediaminetetraacetic acid (EDTA) and phosphoric acid. The last corrosion layers were then stabilised with sodium benzoate.

Once it was established that acetic acid had contributed to the formation of the corrosion products that contained acetate, the project conservator used acid-free cardboard boxes to store the cameras, and removed the cellulose acetate films for storage in a separate box. To provide isolation, the black cellulose acetate textiles were separated from their metal support by a layer of acrylic (Paraloid B-72, 5% solution in toluene). In addition, a permanent acetic acid measuring device was placed in the showcase and the storage boxes (A-P-Strips, IPI, Rochester Institute of Technology, Rochester, NY) together with pollution absorbers (Zinc oxide and active charcoal textile).

In order to protect the most sensitive components made of magnesium/aluminium and magnesium/zinc alloys from an aggressive environment (organic acid) and humid atmosphere, the surfaces were coated with 5% Paraloid B-72 in toluene. All moving parts of the camera were coated with mineral oil, and mineral wax was used to coat the static components.

After conservation was complete (see Figure 9), the pigeon cameras were returned to the Swiss Camera Museum in Vevey and have been on exhibit there ever since with no corrosion problems noted (Berger 2008).

Conclusion

The conservation of three pigeon cameras was a close collaboration between AMC, LRC and LIC. The analytical results showed that different parts of the cameras were made from different metal alloys (magnesium/aluminium; zinc/magnesium, zinc/copper and aluminium). Only the magnesium alloys were covered with a thick corrosion layer. It is known that earlier magnesium alloys are not pure enough to be resistant against corrosion. The white corrosion layer turned out to be a mixture of magnesium acetate and magnesium carbonate hydroxide hydrate. The analytical study of the materials used for the manufacture and storage of the cameras showed that the corrosion was mainly due to the presence of acetate in films and textiles, leading to the release of acetic acid, combined with free acids originating in the cardboard boxes. These results were important for selecting the treatment and long-term preventive conservation strategy.

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Figure 8. A pigeon camera before treatment



Figure 9. A pigeon camera after treatment

Materials

Paraloid B-72, Paraffin oil, wax Cosmoloïd H 80, EDTA and anionic soap

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