

When Glass and Metal Corrode Together, II: A Black Forest *Schäppel* and Further Occurrences of Socoformacite

Gerhard Eggert* and Anne Bühner
State Academy of Art
and Design Stuttgart
Stuttgart, Germany
gerhard.eggert@abk-stuttgart.de

Bruno Barbier and Harald Euler
Steinmann-Institute of Geology,
Mineralogy, and Paleontology
University of Bonn
Bonn, Germany

Abstract

In 2008, two cases of sodium copper formate acetate (socoformacite) as copper/glass corrosion products on objects exposed to wood were reported. This phenomenon is not rare. Socoformacite has now been found in the contact zones of corroding glass and copper alloys on a Black Forest *Schäppel* decorated with hollow glass beads on wires, a ball-shaped ornament (for a Christmas tree) with silvered copper spirals, early Limoges enamels on copper, the brass mat of a glass-framed daguerreotype, a glass figure of the late 16th century with interior wire, and a 13th-century glass cabochon with a silver mount. To prevent such corrosion, objects in which copper alloys are in contact with corroding soda glass should be stored dry like “sick” glasses, with metal and glass isolated by coatings (if possible) and protected from carbonyl pollutants.

Keywords: glass corrosion, copper alloys, sodium copper formate acetate

Introduction

More than two centuries of scientific analysis of copper corrosion products on artifacts seems not to have exhausted the subject. In 2002, another new product was identified: a pale blue corrosion product on copper-alloy artifacts containing sodium and copper in a ratio of about 1:1, estimated from high-resolution X-ray photoelectron spectra (Trentelman and others 2002). With one exception, all of the samples in this report were from archaeological finds that may have come from soda-rich soils (e.g., in Egypt) or that may have been treated decades ago with alkaline solutions (sodium sesquicarbonate treatment against bronze disease, or electrochemical or electrolytic reduction in caustic soda; see Plenderleith and Werner 1971).

Raman spectroscopy of such a product detected both formate (methanoate) and acetate (ethanoate) anions in the crystalline compound. Because wood continuously emits traces of formic and acetic acid (ester bound in its hemicelluloses) into the air, the mixed formate/acetate probably results from exposure to pollutant emissions (e.g., from wooden display or storage components) over long periods. According to Trentelman and others (2002), the formula of this sodium copper formate acetate (socoformacite) can be given as $\text{NaCu}(\text{HCOO})_{1+X}(\text{CH}_3\text{COO})_{2-X}$ with X (if integer) = 0 or 1. X-ray diffraction (XRD) gives a unique “fingerprint” pattern and is therefore the preferred method of identification. Data for comparison are

given in the literature (Trentelman and others 2002, figure 3 and table 1; Eggert and others 2008, table 1). Unfortunately, they cannot be found in the Powder Diffraction File or in crystal structure databases: the unit cell of socolformacite crystals is unknown because no single crystals of sufficient size could be prepared synthetically or found among the corrosion products so far.

At the ICOM Committee for Conservation triennial meeting in New Delhi (Eggert and others 2008), two objects with socolformacite corrosion that had been neither soil-logged nor treated in (caustic) soda solutions were presented:

1. A limewood box of board games made in the 1670s for Countess Hedwig-Sophie of Hesse-Kassel. Some of the turquoise enamel (made from saline plant ash, about 13%–16% m/m Na₂O, wavelength-dispersive X-ray microprobe) used for the decoration of the silver-alloy (about 5.5% m/m Cu, atomic absorption spectrometry) backgammon fields had flaked off. In some of the now open silver grooves, where there was formerly enamel (and only there!), socolformacite was identified by XRD.

2. A roughly century-old Chinese theater hat (Ethnological Museum of Heidelberg, 30406) that has long been stored in a cupboard made of oak. The hat consists mainly of silk stabilized with cardboard. Silvered copper wire and glass beads were used as decorative elements. One metal spiral was covered with a light green-blue corrosion product where it was in direct contact with an apparently weathered glass bead, showing iridescence and crizzling.

In these cases, the sodium in socolformacite clearly came from active soda glass corrosion (end product: sodium carbonate if no carbonyl or acid pollutants are present). The corroding glass affected the corrosion of copper alloys. To see how rare this type of corrosion is, conservators and students from the program in Stuttgart were asked to look for possible samples. Within three years, seven further examples were found on objects of very different types and ages. They are catalogued below to illustrate the diversity of the hitherto unrecognized phenomenon.

A Black Forest *Schäppel*

Schäppels (from medieval *capa*, “headdress”) are traditional girls’ headdresses worn in the Black Forest and elsewhere on high ecclesiastical and family holidays such as those that mark baptisms and weddings. They are found in many forms, each specific to a certain occasion and village. Derived from medieval times and the crown of Mary, they usually have a basketlike form and are made of reflecting or colored glass balls, brass plates, mirrors, metal wire, paper decorations, artificial flowers, and similar decorative materials. Lampworked glass beads came either from Lauscha (Thuringia), Germany, or from Gablonz, Bohemia (now Jablonec nad Nisou, Czech Republic). The Black Forest *Schäppel* from the Landesmuseum Württemberg, Stuttgart (VK 13221b; Bühner 2009), was made in the late 19th century, possibly in St. Georgen (Fig. 1). Many beads show signs of corrosion or are lost. In some



Figure 1
Black Forest *Schäppel*. H. about 25 cm.
(Photo: Anne Bühner)



Figure 2
Spiraled wire from *Schäppel* corroded by contact with glass (detail of object in Figure 1). (Photo: Anne Bühner)

spots, the spiraled “bouillon” wires are close to glass covered with turquoise copper corrosion (Fig. 2). Two samples were analyzed by XRD, and both contained socoformacite, one together with cuprite (Cu_2O), an ubiquitous red corrosion product on copper alloys exposed to air. *Schäppels* from the collection of the Badisches Landesmuseum Karlsruhe also seem to show signs of copper corrosion, but they have not yet been analyzed.

To protect these valuable objects from dust, *Schäppels* were traditionally stored in special wooden or paper boxes or in wooden cupboards.

A Ball-Shaped Christmas Ornament with Wires

Interestingly, another occurrence of socoformacite has been confirmed by XRD on a ball-shaped ornament for a Christmas tree from the Badisches Landesmuseum Karlsruhe collection (no inventory number). The hollow glass ball (Fig. 3), which may have been made in Lauscha in the late 19th or early 20th century, is mirrored on the inside and decorated with spirals of silvered copper wire. In 2002, corrosion products on the wires were stripped with an aqueous disodium ethylenediamine tetraacetate (Na_2EDTA) solution. Seven years later, copper corrosion appeared again, and a sample was taken. It is unlikely that the corrosion is related to the treatment because the corrosion is clearly limited to the contact zone between metal and glass. This demonstrates that visible amounts of socoformacite do not need decades to form. Apparently the ornament was continuously exposed to an atmosphere favoring socoformacite formation.

Early Limoges Enamels on Copper

The Museum für Angewandte Kunst Frankfurt has two objects in its enamel collection that have been affected by socoformacite corrosion (samples courtesy of Andrea Schwarz). A small copper fitting (D. 6.3 cm) in quatrefoil form with *émail champlevé* depicts a kneeling angel holding a band with the Gothic letters for “Matthew” (6341). The museum catalog (Zinnkann 2004, p. 50) dates the object to the early 14th century. Two samples of the turquoise and green corrosion (Fig. 4) outlining the border between copper and enamel contained both socoformacite and a newly detected basic copper formate, $\text{Cu}_2(\text{OH})_3\text{HCOO}$ (Euler and others 2009).



Figure 3
Corroded wires on a ball-shaped ornament for a Christmas tree. D. 5 cm. (Photo: Anne Bühner)



Figure 4
Turquoise and green corrosion at border between enamel and copper on Saint Matthew fitting. (Photo: Andrea Schwarz)

The same compounds were also detected on an *émail peint* object. The enameled copper plaque (WMH 1, 17.8 cm x 13.4 cm) depicting the Adoration of the Magi was painted by Léonard Nardon Pénicaud in about 1500 (Zinnkann 2004, pp. 55–57). The blue and violet enamels in particular show clear signs of deterioration. Blue and green

corrosion samples came from the copper support, cracks in the enamel, and the metal frame.

Problems with carbonyl pollutants in this collection are also indicated by one occurrence of thecotrichite, $\text{Ca}_3(\text{CH}_3\text{COO})_3\text{Cl}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ (Gibson and others 2005), an acetate-containing corrosion product of calcareous materials.

A Daguerreotype

A framed daguerreotype from about the 1850s (donated to science by Pau Maynés, Barcelona) in an original wooden box with clasp and hinge covered with embossed leather was the unexpected location of another occurrence. As is usual, the package consisted of a halogen-sensitized polished silvered copper plate (carrying the image of a lady), a brass frame mat, and a cover glass. Such cover glasses can undergo severe corrosion. Barger and White (2000, p. 167) mentioned a basic sodium copper carbonate, $\text{Na}_3[\text{Cu}_2(\text{CO}_3)_3(\text{OH})] \cdot 4\text{H}_2\text{O}$, as one of many detected corrosion products. This is probably a glass/copper corrosion product (Eggert 2010). It can form at an even lower pH (hydrogen carbonate solution, pH about 8.4)



Figure 5
Glass-framed daguerreotype with corroded brass mat. H. (box) 9.2 cm. (Photo: Margarete Eska)

than another glass/copper corrosion product, chalconatronite, $\text{Na}_2[\text{Cu}(\text{CO}_3)_2] \cdot 3\text{H}_2\text{O}$ (carbonate/hydrogen carbonate buffer, pH about 10.3).

The brass mat showed large green to turquoise areas on the upper side, close to the glass (Fig. 5). As in the case of the Limoges enamels, socoformacite was probably identified in a sample from the glass side, together with the basic copper formate, $\text{Cu}_2(\text{OH})_3\text{HCOO}$ (Euler and others 2009).

A Handstein Glass Figure

The development of mining in late medieval and early modern times influenced the decorative arts. So-called *Handsteins* (German for “hand stone”) combined impressive ore samples with goldsmith’s work as mounts and figures depicting religious or mining scenes. Such a *Handstein* combined from various ores, created by Caspar Ulrich in the late 16th century, is in the collection of the Kunsthistorisches Museum, Vienna (KK 4144, H. 28.9 cm). It includes 17 lampworked colored glass figures for scenes of Saint George slaying the dragon on the top level and mining on the middle and lower levels. A small kneeling female figure made of blue glass that is now heavily corroded had cracks in her arm. Out of the cracks grew green to blue efflorescences (Fig. 6), with socoformacite as the only crystalline corrosion product (Bernhard 2008).



Figure 6
Efflorescence at cracks in arm of glass figure. (Photo: Wibke Bernhard)



Figure 7
Corroded glass cabochon on Otto-Adelheid-Gospel, with green efflorescences on bezel. (Photo: Rainer Richter)

After the corrosion was removed, an interior copper-alloy support wire could be seen.

The interior of the *Handstein* is constructed of wood, and the Vienna *Handstein* collection has long been stored in wooden display cases. Measurements by the Technical University of Vienna found 10- to 20-fold acid concentrations in the cases as compared with the room air (up to $149 \mu\text{g m}^{-3}$ formic acid and up to $1.121 \mu\text{g m}^{-3}$ acetic acid). Happily, no other *Handstein* showed signs of carbonyl-induced corrosion.

A Glass Cabochon with Mount

The cover of the Otto-Adelheid-Gospel in the collegiate church of Quedlinburg shows an inset with a carved ivory panel (Byzantine, late 10th century) and locally made silver-gilt filigree work (about 1220–1230; Kötzsche 1993). A deteriorating green glass cabochon imitating a gem is set in a silver-gilt bezel. Green efflorescences on the apparently alloyed silver (sample courtesy of Rainer Richter) proved to be socoformacite (Fig. 7). The gospel had formerly been displayed in a case in which high emissions of acetic acid were analytically verified.

Recommendations

In the reported cases, corrosion products formed on metals only where they were in contact with corroding glass with hygroscopic alkaline surface films. This phenomenon

is not at all rare, and the Christmas ornament illustrates that corrosion will reoccur if the corrosive agents are not removed from the atmosphere. In order to best preserve the metal parts, humidity should be kept as low as possible, but the hydration layer of the corroding glass sets a lowest limit. Therefore, objects consisting of glass and copper alloys in contact with each other should be stored at the same relative humidity (RH) levels as “sick” glasses. Most recommendations are between 35% and 45% RH (Kunicki-Goldfinger 2008, p. 54). The source of the carbonyl pollutant should be removed (if it is not part of the object). Wood and wood products may no longer be considered safe for the storage or display of glasses and metals. If the source of the pollutants cannot be removed, their concentration should be lowered by absorbents (e.g., alkali-impregnated charcoal cloth). Absorbents must, of course, be replaced regularly. Where there is only loose contact between metal and glass (e.g., beads on a wire), the contact can be prevented by using a surface coating. Paraloid B-72 is known to work on both materials.

Research on metal/glass corrosion is still in its infancy. Other corrosion products (including unknown phases) have been found and need further study (Eggert 2010). For instance, potash glasses could yield potassium (K^+) compounds, and other anions (e.g., sulfate) are possible. Therefore, when cleaning an object exhibiting contact corrosion, efflorescences should always be sampled.¹ They tell something about the (storage) history of the object and may add to our general knowledge in order to improve preventive conservation.

One day, this corrosion phenomenon should become extinct. May future generations of conservators know of it only from historical literature such as this paper!

1. Since not all corrosion products can routinely be found in the Powder Diffraction File, samples should be sent to specialized conservation scientists for identification. G.E. can be contacted by e-mail: gerhard.eggert@abk-stuttgart.de.

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