



Chemical Education

A CHIMIA Column

Topics for Teaching: Forensic Chemistry in Schools

Visualization of Latent Fingerprints on Aluminum

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Abstract: For aluminum, a new visualization method is presented in which copper is deposited electrochemically. The fingerprint on the aluminum (trace carrier) serves as an insulator as it prevents direct contact between electrolyte and aluminum. The decisive factor is the choice of an ammoniacal copper sulfate solution, which acts as a corrosion inhibitor due to the ammonia molecules. This enables uniform copper deposition on aluminum and thus the development of a clearly defined negative image.

Keywords: Aluminum · Chemical education · Electrochemical method · Visualization latent fingerprints

Aluminum not only plays a special role in the galvanic series of metals, but also in forensic research. It has a standard potential of -1.67 V but does not react with weak acids and bases or metal salt solutions that have a more positive standard electrode potential. Therefore, forensic methods based on a reaction with aluminum as the trace carrier cannot be used. The reason for this behavior is the protective oxide layer – consisting of di-aluminum trioxide Al_2O_3 , aluminum trihydroxide $\text{Al}(\text{OH})_3$ and aluminum oxide hydroxide $\text{AlO}(\text{OH})$ ^[1] – which is formed as soon as aluminum comes into contact with atmospheric oxygen. If aluminum objects are found at the scene of the crime, the powder method^[2] or the cyanoacrylate fuming method^[3] are usually used to visualize the latent fingerprints. These methods are easy to use, but they also have a decisive disadvantage, because both methods only allow the investigation of dry trace materials. In the following, the electrochemical method is presented, which is suitable for wet and electrically conductive trace material. It will be shown which problems arise when aluminum is used as a trace carrier and how this method can nevertheless be used in school lessons as well.

The investigation and visualization of latent fingerprints on different metals has increasingly moved into the focus of forensic research in recent years. Firing cartridge cases,^[4] but also coins^[5] and knives^[6] are used as trace carriers for the different methods in order to establish a connection between the murder weapon and the perpetrator. An electrochemical process was developed which enables visualization by means of metal deposition.^[7] The trace carrier on which the latent fingerprint is located, is placed in a more noble metal salt solution. The metal is deposited on the trace carrier, whereby the places where the fingerprint residues are located do not react. The sebaceous components are not soluble in the polar solvent and the metal has no direct contact with the electrolyte at these areas. As a result of this experiment a negative impression can be seen. The process of the described method is shown in Fig. 1.

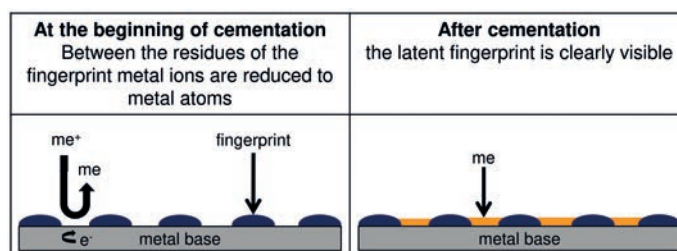
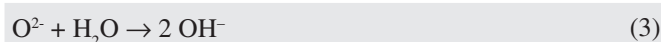
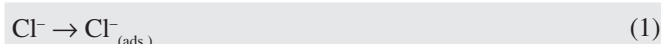


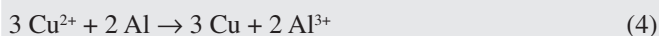
Fig. 1. Schematic representation of the metal base (electrically conductive base) and the fingerprint on it (cross-section), left: at the beginning of cementation, right: after cementation is complete.

In a previous article, the authors have shown that different metals can be examined in this way reproducibly with means available to schools.^[8] Aluminum was not taken into consideration because it has a very low electrical conductivity due to its oxide layer and thus makes visualization impossible. To expose the elementary aluminum, a way must be found to break down the oxide layer. This is the case in strong bases,^[1] since the protective oxide layer cannot form or reacts immediately after its formation. However, the reaction brings a violent hydrogen development^[1] and thus prevents metal deposition. Alternatively, the use of chloride ions in neutral aqueous solutions can be an option. Hydrogen is also produced, but on a smaller scale, which makes copper deposition possible at the same time. In the experiment this reaction is caused as follows: An aluminum plate is provided with a sebaceous fingerprint. It is then placed in a 0.2 molar copper(II) chloride solution for five minutes. Copper deposition can be achieved by the reaction of the chloride ions with the aluminum oxide. However, this cementation reaction is not uniform, but takes place according to the mechanism of the so-called pitting corrosion.^[9] This is caused by impurities (e.g. scratches and cut edges) and heterogeneous inclusions in the aluminum oxide layer, since a reaction is particularly favored at these points.^[10] The authors propose the following didactically reduced reaction mechanism: In the first reaction step, chloride ions are adsorbed onto the aluminum oxide (Eqn. 1). These then react with the aluminum ions of the oxide layer to form the tetrachloroaluminate complex (Eqn. 2). The remaining oxygen ions of the oxide layer react with water molecules to form hydroxide ions (Eqn. 3). Now the elementary aluminum has direct contact to the electrolyte and copper deposition takes place (Eqn. 4). In addition, due to the negative normal potential, aluminum atoms react with water molecules to form aluminum ions, hydroxide ions and hydrogen molecules (Eqn. 5).



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Copper pits form on the metal plate and the experimental result shows a poorly visible fingerprint (Fig. 2).

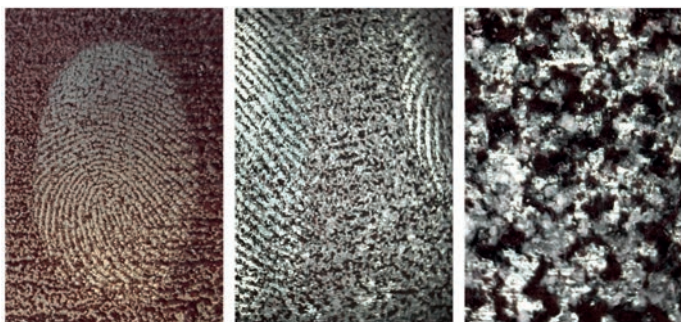


Fig. 2. Copper deposition on aluminum; reaction conditions: 0.2 molar copper(II)-chloride solution and 5 min. reaction time; from left to right: total fingerprint, partial section of the fingerprint at 50x magnification and close-up of the pitting areas (200x magnification).

The key to success lies in the use of corrosion inhibitors. During corrosion in humid environments, chemicals are added to the corrosion medium in order to reduce the corrosion rate.^[11] Because of the large number of inhibitors and their not yet completely understood mechanisms of action, they are classified in the literature according to different category systems. They are classified as physical and chemical inhibitors.^[12,13] Physical inhibitors adsorb reversibly on the metal surface, while chemical inhibitors react either with the metal surface of the metal to be protected or with the attacking components of the corrosion agent.^[12] All the theories have the assumption in common that corrosion inhibitors either adsorb on the metal surface or react with the corrosive substance and thus lead to a reduced corrosion rate. Regardless of which classification system is used as the basis, the prerequisite for adsorption of the inhibitor molecules on the metal surface is the presence of π electrons.^[14] This is a necessary condition, but it is not sufficient, *i.e.* not every substance with these properties acts as a corrosion inhibitor. Consequently, inhibitors must be determined experimentally and the required concentration in relation to the metal and the corrosive medium must be determined by the weight loss of the sample sheet or by a current–voltage curve.^[13,14] According to Wranglén,^[11] the electrolyte determined experimentally in our research, which contains ammonia molecules, is an adsorption inhibitor that forms a coordinative bond to the metal surface. To visualize the fingerprint, electrolysis is performed using a 0.2 molar ammoniacal copper sulfate solution. The aluminum plate is again provided with a sebaceous fingerprint and is connected as a negative pole. A graphite foil is used as the counter electrode. At a voltage of 3 V (200 mA) the electrolysis is stopped after five minutes. The result shows a uniform copper deposition and thus a negative impression of very good

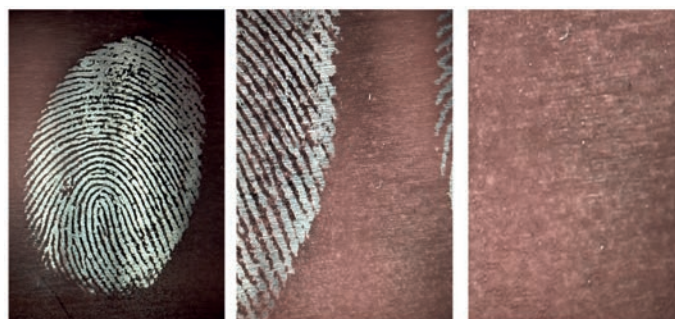


Fig. 3. Electrolytic copper deposition on aluminum; reaction conditions: 0.2 molar ammoniacal copper sulphate solution; 3 volts; 200 mA; 5 min. reaction time; from left to right: total fingerprint, partial fingerprint section at 50x magnification and close-up of the uniform copper deposition (200x magnification).

quality (Fig. 3). During the test, no hydrogen development is detectable, thus a uniform, electrolytically forced copper deposition is possible. For the first time, this test makes it possible to investigate latent fingerprints on aluminum (even in school chemistry lessons) using the electrochemical method.

With regard to school chemistry, the presented topic offers a motivating context against which curricular contents such as electrochemistry, pitting corrosion and (corrosion) inhibitors can be developed. The topic is a small component of the forensic school experiments developed at the Freiburg University of Education. Further experiments on these visualization methods will be published in due course.

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