
Understanding how silver objects tarnish

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The following activity is for heritage professionals who want to learn about tarnish on silver. It is part of the Canadian Conservation Institute's [Care of Metals in Collections Workshop](#). A laboratory and ventilation are not required for this activity, and it can be easily undertaken in a classroom, museum workspace or even at home.

Learning objectives

By understanding how silver tarnishes, heritage professionals will be able to:

- Recognize the early stages of silver tarnishing
- Identify and minimize use of materials or exposure to environments that cause silver to tarnish

Background

When silver is exposed to sulfur-containing gases in the air, it discolours and then darkens as it reacts with the gas to form a surface layer of tarnish. This process is called tarnishing, as explained below in [The science of silver tarnish and its cause](#). Protecting silver objects from tarnishing is an important task for heritage professionals.

Tarnish generally disfigures a silver object. It can be removed by polishing or other techniques, but this cleaning can be labour intensive. Moreover, each time an object tarnishes and is cleaned, some silver is lost. On silver-plated objects, polishing can damage the thin layer of silver plating, or even remove it entirely. Hence, if possible, it is best to prevent the object from tarnishing, especially for museum or heritage pieces.

If a silver object is to be kept from tarnishing, it must be protected from sulfur-containing gases. These gases come from a variety of sources. It may be impossible to prevent silver from tarnishing when it is on open display in a historic house. Even placing silver in a sealed display case may not protect it if the display case is made from inappropriate materials or if it is not airtight enough.

Activity: how to make a silver object tarnish

This hands-on activity outlines the procedure and required materials to demonstrate how quickly tarnish can form on silver. The activity involves exposing polished silver to a freshly hard-boiled egg.

Equipment and materials required to make silver tarnish

- Freshly hard-boiled egg
- Knife to cut egg
- Silver samples such as silver-plated items or small pieces (coupons) cut from silver sheet
- Precipitated calcium carbonate (precipitated chalk)
- Transparent container that can be sealed (e.g. plastic box with a good lid, plastic box inside a sealable plastic bag)

Procedure to make silver tarnish

1. Hard boil an egg
2. Clean the silver with mild soap and water to remove any dirt and grease
3. Polish the silver with precipitated calcium carbonate (as described in CCI Note 9/7 [Silver – Care and Tarnish Removal](#))
4. Place one or more silver samples in the transparent container
5. Remove the shell from a freshly hard-boiled egg, preferably still warm
6. Rinse the egg with tap water and leave outer surface wet
7. Cut the egg into four pieces with the knife
8. Place the egg into the transparent container with the silver
9. Cover the box or place it inside a sealable plastic bag
10. Note the time and date
11. Monitor the surface of the silver for the next one to two hours
12. Discard egg after activity is finished

Results of this activity

After 5 to 30 minutes, the silver sample should first turn yellow. (The sooner the egg is used after hard boiling, the faster the tarnishing reaction. Ideally, the egg should be used while it is still warm.) At longer times, the colour changes from yellow to red, blue or black. The sulfur-containing gas that is causing the tarnish to form is hydrogen sulfide given off by the hard-boiled egg. An example of this colour change is shown in Figures 1a to 1c.



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Figure 1a: A transparent box containing a silver-plated spoon and a hard-boiled egg: initial exposure.



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Figure 1b: A transparent box containing a silver-plated spoon and a hard-boiled egg: after 40 minutes.



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Figure 1c: A transparent box containing a silver-plated spoon and a hard-boiled egg: after 1 hour and 22 minutes.

Suggestions for additional testing

Silver plate versus sterling silver

Repeat the activity by comparing the tarnishing rate of two samples in the same container: (1) a silver-plated object or a coupon of pure silver and (2) a sterling silver object or coupon. Sterling silver (an alloy with 92.5% silver and 7.5% copper) tarnishes faster than the pure silver found on a silver-plated object. An example of this activity is shown in the following [time-lapse video](#), which includes photographs recorded every minute for about 90 minutes. It compares the tarnishing of a silver-plated spoon to a sterling silver knife.

The higher tarnishing rate of sterling silver is due to the copper in the silver-copper alloy. Copper is more reactive than silver (Graedel 1992). In general, the tarnishing rate of silver-copper alloys increases with increasing copper content (Selwyn 1990).

Homemade versus commercial silver polishes

Repeat the activity by comparing the tarnishing rate of two samples in the same container: (1) a silver coupon or silver-plated object cleaned with a homemade silver polish (precipitated calcium carbonate and water) and (2) a silver coupon or silver-plated object cleaned with a commercial silver polish.

Most commercial silver polishes contain a tarnish inhibitor, which, as the name suggests, slows down or inhibits the tarnishing of the silver (Selwyn and Costain 1991). The presence of a tarnish inhibitor in a commercial polish is implied by phrases such as “tarnish preventative,” “tarnish guard,” “anti-tarnish ingredient,” “tarnish retardant” or “prevents tarnish” on the package labelling. If there is a tarnish inhibitor in the commercial polish used in this activity, then the silver cleaned with it will tarnish more slowly than the silver cleaned with a homemade polish containing precipitated calcium carbonate.

Tarnish inhibitors are organic molecules that attach to the silver surface through silver-sulfur bonds, forming a thin transparent layer. This layer, with its wax-like properties, repels water and tarnishing gases and so protects the silver to some extent. But when the silver does tarnish, the tarnishing may be uneven, and the object may look more disfigured than one with a thicker but uniform layer of tarnish. Moreover, the wax-like layer may interfere with lacquering (Lins and McMahon 1993). For these reasons, commercial polishes with tarnish inhibitors tend to be avoided in museums.

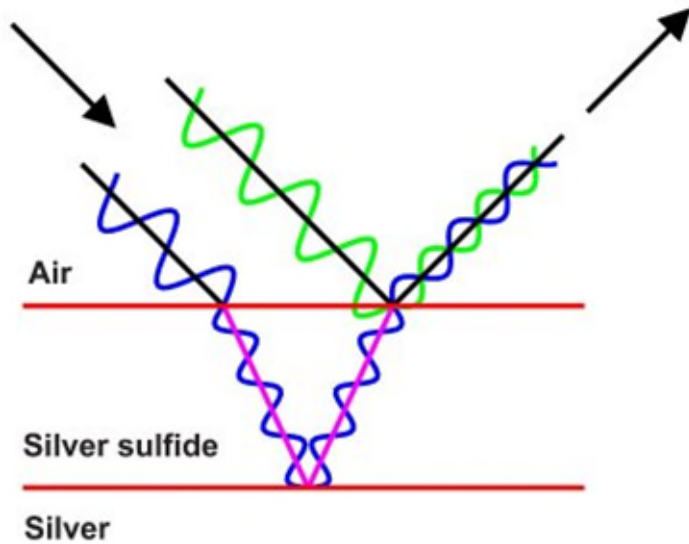
The science of silver tarnish and its cause

Tarnish on silver

Tarnish on pure silver is the compound silver sulfide (Ag_2S , mineral acanthite), which forms when the silver reacts with sulfur-containing gases in the air. Tarnish on sterling silver also contains copper sulfide (Cu_2S) (Graedel 1992). The most common sulfur-containing gas is hydrogen sulfide (H_2S), which is the one given off by a hard-boiled egg.

Interference colours

The colour of tarnish on silver changes as tarnishing proceeds. This is due to a phenomenon called “thin film interference.” As light hits the thin film of tarnish on the silver, it splits; some of it reflects off the top surface, and some of it reflects off the silver under the tarnish (Figure 2).



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Figure 2: As light hits the silver sulfide tarnish layer, some of it reflects off the top surface, and some of it passes through and then reflects off the underlying silver layer. These two different paths for the light result in light interference and produce different colours on the silver surface, depending on the thickness of the silver sulfide tarnish layer.

When the light from the top and the bottom of the tarnish recombines, some of the colours are lost through interference. The colour that remains depends on the thickness of the tarnish layer. In the early stages of tarnishing, as the thickness grows from 10 to 100 nanometres (nm), the colour changes from yellow through red-brown to blue. For thicknesses greater than about 100 nm, the colour is black, the true colour of silver sulfide (Selwyn 2004). Figure 3 contains an example of a silver-plated cup with interference colours.



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Figure 3: A silver-plated cup showing interference colours from a thin layer of tarnish formed over several years while the cup was sitting in the open air at the Canadian Conservation Institute.

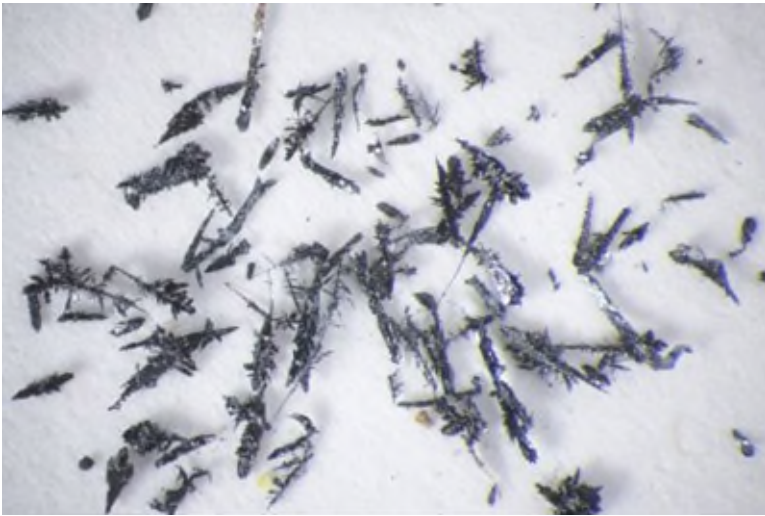
Whisker formation

Sometimes silver reacts with sulfur-containing gases to form three-dimensional whiskers (Figures 4a and 4b).



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Figure 4a: Whiskers of silver sulfide on silver inlays in steel.



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Figure 4b: Silver sulfide whiskers removed from silver inlays in steel.

Although several examples of whisker formation have been noted in the conservation literature, it is not known why tarnishing sometimes produces whiskers instead of an even layer of tarnish (Selwyn 2004, Eggert et al. 2008, Sease et al. 1997).

How quickly silver tarnishes

The rate that silver tarnishes depends on the concentration of sulfur-containing gases (such as hydrogen sulfide) in the air. In a museum setting, where a dark layer of tarnish may take months or years to form, the hydrogen sulfide concentration is typically between 86 and 600 parts per trillion (ppt) (Ankersmit et al. 2005). (One part per trillion of a gas means there is 1 molecule of that gas in 1 trillion, or 10^{12} , molecules of air.) Silver exposed to a freshly hard-boiled egg tarnishes within minutes rather than months, showing that the concentration of hydrogen sulfide from the egg is much higher than within a typical museum setting.

Tarnish grows more quickly on silver that has been freshly polished than on silver that has already tarnished. Thus a layer of tarnish, as unappealing as it might appear, actually helps to protect the silver against further tarnishing. For this reason, it is usually recommended that tarnished silver be left unpolished unless cleaning is required for exhibit or display.

Relative humidity (RH) also affects the tarnishing rate. For a given concentration of hydrogen sulfide, silver tarnishes faster as the RH climbs. As a result, silver is best stored in dry conditions (below 50% RH). For more information on preventive conservation strategies for silver, see [Metals](#).

Sources of tarnishing gases

Tarnishing gases may originate from the following sources (Ankersmit et al. 2005, Benson 2012, Selwyn 2004, Selwyn 1990):

- Clays (e.g. certain modelling clays)
- Drywall (poor quality)
- Foods (certain ones such as eggs)
- Glues (protein-based)
- Heating fuel (especially coal-based)
- Paints (certain ones)
- People (intestinal gas emissions containing hydrogen sulfide)
- Plaster casts (made with gypsum)
- Pulp-and-paper industries
- Sewer gases
- Sulfur (elemental sulfur), sometimes used for:
 - Adhesives
 - Cement
 - Grout
 - Inlays in furniture
 - Munitions
- Volcanoes and hot springs
- Vulcanized rubber objects such as:
 - Ebonite
 - Latex gloves
 - Molding material (polysulfide rubber)
 - Pencil erasers
 - Rubber bands
 - Rubber gloves
 - Rubber o-rings
 - Rubber stoppers
 - Vulcanite
- Water (some natural well water and bogs)
- Wood (recovered from anaerobic environments)
- Wool, wool felt

Additional effects of sulfur in eggs

When an egg is heated, the proteins in the egg white produce hydrogen sulfide gas (McGee 1984). This is the gas that causes the silver to tarnish in the activity. If some of the gas reacts with iron in the yolk, it forms brown iron(II) sulfide (FeS), producing a green-gray layer on the yolk of a hard-boiled egg as shown in Figures 5a and 5b. (To minimize the green-gray layer, cook the eggs as little as possible—just enough to set the yolk—and cool rapidly after cooking.)



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Figure 5a: One view of the surface of a yolk in a hard-boiled egg showing the green-gray layer of iron(II) sulfide (FeS).



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Figure 5b: Another view of the surface of a yolk in a hard-boiled egg showing the green-gray layer of iron(II) sulfide (FeS).

Acknowledgements

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Suppliers

Note: The following information is provided only to assist the reader. Inclusion of a company in this list does not in any way imply endorsement by the Canadian Conservation Institute.

Precipitated calcium carbonate (precipitated chalk)

Precipitated calcium carbonate is available from chemical supply companies such as Fisher Scientific (calcium carbonate powder). Precipitated calcium carbonate is also available in small quantities from some conservation suppliers such as Talas (calcium carbonate ultrafine) and Conservation Support Systems (precipitated calcium carbonate).

- [Fisher Scientific](#)
- [Talas](#)
- [Conservation Support Systems](#)

Silver

Thin sheets of pure silver (e.g. foil, 0.1 mm thick) are available from [Sigma-Aldrich](#).

Sterling silver

Sterling silver is available from jewellery suppliers such as [Lacy & Company Ltd](#).

References

- Ankersmit, H., N. Tennent and S. Watts. "Hydrogen Sulphide and Carbonyl Sulphide in the Museum Environment—Part 1." *Atmospheric Environment* 39 (2005), pp. 695–707.
- Benson, P.L. "Some Unusual, Hidden, Surprising, or Forgotten Sources of (Possible) Sulfur Contamination in Museums and Historic Structures." *AIC Objects Specialty Group Postprints* 19 (2012), pp. 85–107.
- Eggert, G., A. Wollmann and B. Schwahn. "When Glass and Metal Corrode Together." In J. Bridgland, ed., *ICOM-Committee for Conservation, 15th Triennial Meeting, New Delhi, India*, vol 1. New Delhi, India: Allied Publishers, 2008, pp. 211–216.
- Graedel, T.E. "Corrosion Mechanisms for Silver Exposed to the Atmosphere." *Journal of the Electrochemical Society* 139 (1992), pp. 1963–1970.
- McGee, H. *On Food and Cooking*. New York, NY: Charles Scribner's Sons, 1984, p. 69.
- Lins, A., and N. McMahon. "The Inhibition of Silver Tarnishing." In S. Aoki, ed., *Current Problems in the Conservation of Metal Antiquities*. Tokyo, Japan: Tokyo National Research Institute of Cultural Properties, 1993, pp. 135–162.

- Sease, C., L.S. Selwyn, S. Zubiato, D.F. Bowers and D. R. Atkins. "Problems with Coated Silver: Whisker Formation and Possible Filiform Corrosion." *Studies in Conservation* 42 (1997), pp. 1–10.
- Selwyn, L.S. "Historical Silver: Storage, Display, and Tarnish Removal." *Journal of the International Institute for Conservation – Canadian Group* 15 (1990), pp. 12–22.
- Selwyn, L. *Metals and Corrosion: A Handbook for the Conservative Professional*. Ottawa, ON: CCI, 2004.
- Selwyn, L. [Silver – Care and Tarnish Removal](#). CCI Notes 9/7. Ottawa, ON: CCI, 2007.
- Selwyn, L.S., and C.G. Costain. "Evaluation of Silver-Cleaning Products." *Journal of the International Institute for Conservation – Canadian Group* 16 (1991), pp. 3–16.