Pacific Silvercloth: Recommendations for Its Use as an Anti-Tarnishing Agent in Silver Collections

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INTRODUCTION

Pacific Silvercloth, a SilverGuard product, is a dark brown, cotton textile which owes its anti-tarnishing qualities to silver particles embedded within the fabric. The particles react with atmospheric pollutants, specifically hydrogen sulfide and carbonyl sulfide (Selwyn 2004). When a silver object is wrapped in Pacific Silvercloth or sealed within a display case with Pacific Silvercloth, the cloth reduces the sulfurous gases in the environment, preventing the formation of sulfur-based corrosion products on the silver object.

Tarnishing Reaction of Silver and Hydrogen Sulfide

$2Ag\ (s) + OH^- + HS^- \longrightarrow Ag_2S\ (s) + H_2O + 2e^-$

Six-Year Natural Ageing Study

Concerns Regarding Use of Pacific Silvercloth

- Commercial product with unknown composition and lifetime.
- Reports of Pacific Silvercloth etching copper objects, causing possible problems for sterling silver.
- Cloudy white surface observed where sterling silver in contact with Pacific Silvercloth (see photo below).
- Previous ageing study conducted by S. Smith (2003) noted suspected plating of silver on metal coupons in contact with Pacific Silvercloth.

White marks on sterling silver from contact with Pacific Silvercloth – Removable with polishing

MATERIALS & METHOD

Aqueous Extraction Method

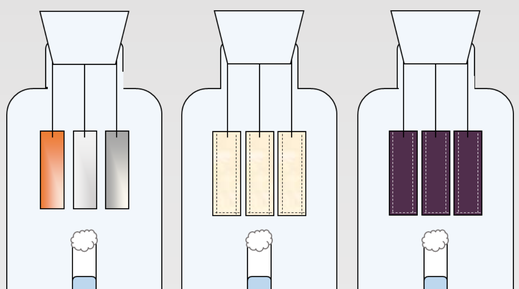
- Extracted Pacific Silvercloth (Silverguard) using variant of the ASTM Standard Test Method for Extractable Matter in Textiles D2257-98 (2012).
- Analyzed extract for presence of salts with conductivity meter, Quantab test strips, lead acetate test strips, and finally inductively coupled plasma optical emission spectrometry (ICP/OES) and ion chromatography (IC).
- Collected solid from extract by evaporation and analyzed using Fourier Transform Infrared spectrometer (FTIR) and X-ray fluorescence (XRF).

Silver Dissolution Method

- Weighed 3 samples of desiccated Pacific Silvercloth (5 x 5 cm) and immersed in 30 % solutions of nitric acid for 3 days.
- Analyzed concentration of silver in solution by ICP/OES.

Accelerated Ageing Method

- Polished metal (0.1 mm silver foil (Sigma-Aldrich); 0.15 mm sterling silver and copper foil (Rio Grande)) with $CaCO_3$, cut into 1 x 3 cm coupons, and degreased in acetone.
- Prepared three trials as illustrated below, in replicates of three.
- Suspended coupons in 250 mL borosilicate glass bottles with borosilicate ground glass stoppers (Thomas Scientific) and sealed with Cosmolloid 80H wax (Talas).
- Weighed bottles before and after ageing to determine air tightness of seal.
- Aged at 60 °C and 100 % relative humidity for 28 days.
- Analyzed coupons by optical microscopy and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS).



No Contact

- Copper, silver, and sterling silver coupons suspended by nylon filament
- Vial of distilled H_2O stoppered by cotton wool

Contact with cotton flannel

- Copper, silver, and sterling silver coupons in sewn cotton flannel pouches suspended by nylon filament
- Vial of distilled H_2O stoppered by cotton wool

Contact with Pacific Silvercloth

- Copper, silver, and sterling silver coupons in sewn Pacific Silvercloth pouches suspended by nylon filament
- Vial of distilled H_2O stoppered by cotton wool

Fabrication of Alternative Anti-Tarnish Cloths

- Washed unbleached cotton flannel following instructions outlined by Montazer et al. (2012) and Tang et al. (2013).
- Deposited silver from solution onto cotton following methods outlined by Montazer et al. (2012) and Tang et al. (2013).
- Analyzed resulting cloths by SEM-EDS.

Sulfur Chamber Testing

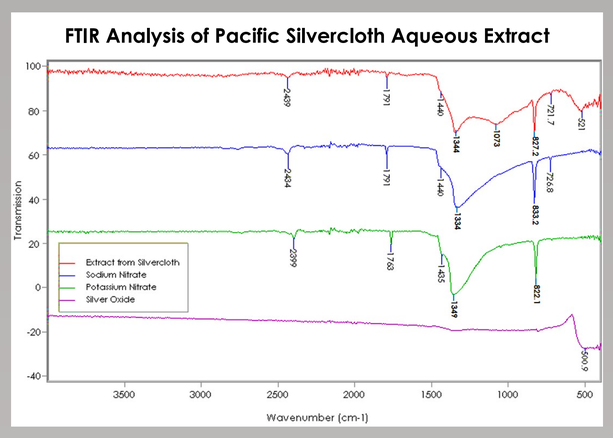
- Method modeled after Gilberg and Cook (1987).
- Polished and degreased 3 x 5 cm sterling silver coupons.
- Sewed pouches from cotton flannel, Pacific Silvercloth, and experimental anti-tarnish cloths.
- Suspended sterling silver coupons in pouches with one uncovered control in a 1 L-vessel with 0.06g thioacetamide (Sigma-Aldrich) and 10 mL of saturated solution of sodium acetate trihydrate (Fisher Scientific).
- Monitored colour change of cloths for 96 hours.
- Quantified colour change in cloths using a Konica Minolta CM-700d spectrophotometer.

ANALYSIS OF SILVERCLOTH COMPOSITION

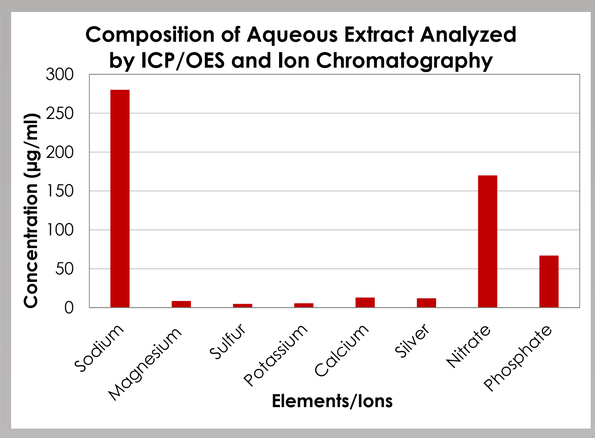
Analysis of the Aqueous Extract of Pacific Silvercloth

- Extract appears to be mixture of sodium nitrate, phosphates, and other salts according to FTIR, ICP/OES, and IC.
- Weak traces of silver in aqueous extract identified by XRF and ICP/OES .

FTIR Analysis of Pacific Silvercloth Aqueous Extract



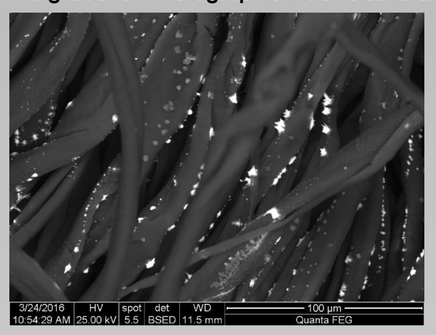
Composition of Aqueous Extract Analyzed by ICP/OES and Ion Chromatography



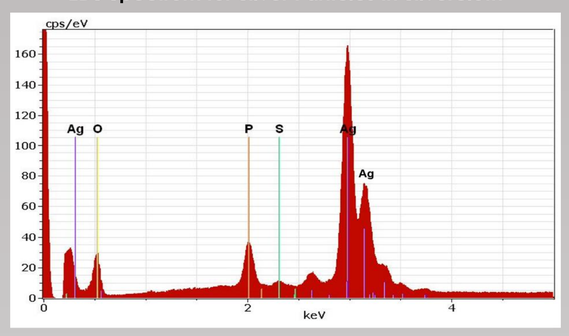
Analysis of the Silver Contained within Silvercloth

- Identified silver particles in Silvercloth as silver phosphate using SEM – potentially made through reaction of silver nitrate and sodium phosphate.
- Determined average amount of silver in Silvercloth, **5200 ± 800 µg Ag/ g Silvercloth**, using ICP/OES to analyze silver concentration dissolved in nitric acid

Scanning Electron Micrograph of Pacific Silvercloth

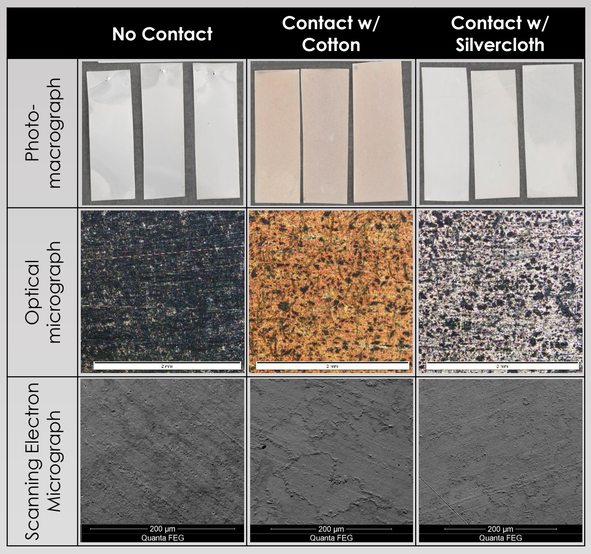


EDS Spectrum for Silver Particles in Silvercloth



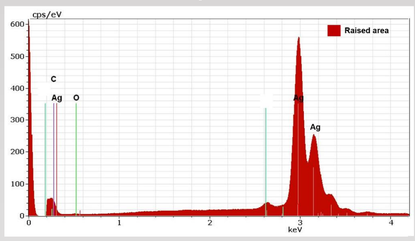
ACCELERATED AGEING OF PACIFIC SILVERCLOTH

ACCELERATED AGEING OF SILVER COUPONS



- White, cloudy tarnish formed on silver coupons in contact with Pacific Silvercloth.
- Yellow tarnish on silver coupons in contact with unbleached cotton flannel due to unexpected iron inclusions.
- Similar tarnish produced by accelerated ageing of silver in direction contact with ash-less filter paper – may be related to ageing of cellulose or to effect of moisture retention at surface of the silver coupons.
- No difference detected by EDS between tarnish products on silver coupons in contact with cotton and Pacific Silvercloth – both composed of oxygen and carbon.

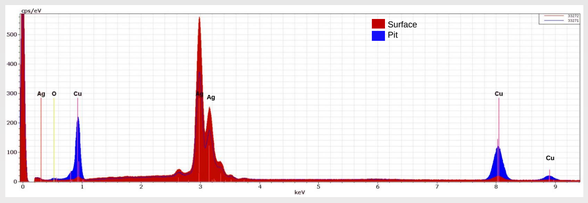
EDS Spectrum of Silver Coupon in Contact with Silvercloth



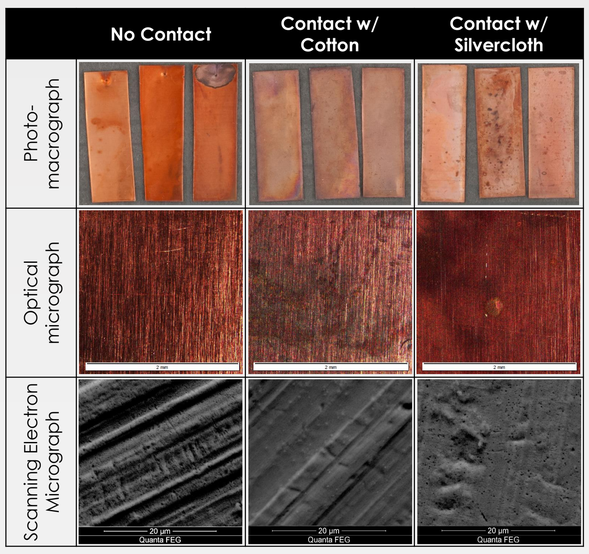
ACCELERATED AGEING OF STERLING SILVER COUPONS

- Sterling silver coupons in contact with cotton and with Pacific Silvercloth appeared to also have cloudy, white tarnish at surface – pattern resembled the textile texture.
- SEM of sterling silver coupons showed pitting at surface of coupons in contact with Pacific Silvercloth in areas with higher copper concentrations.
- May indicate etching of copper-rich areas of the alloy by the formation of a galvanic cell, facilitated by electrolytes contained in Pacific Silvercloth.

EDS Spectra of Sterling Silver Coupon in Contact with Silvercloth Comparing Pitted and Non-Pitted Areas



ACCELERATED AGEING OF COPPER COUPONS



- All copper coupons experienced some degree of tarnishing due to exposure to 100 % relative humidity.
- Bare copper coupons varied greatly in colour – light to dark orange, and purple in locations where humidity condensed.
- Coupons in direct contact with cotton and with Pacific Silvercloth were dull orange with dark purple patches.
- Coupons in direct contact with Pacific Silvercloth slightly more discoloured relative to control groups.
- SEM showed oxygen-based tarnish on all copper coupons.
- Some pitting visible on coupon in contact with Pacific Silvercloth however pits also present on control coupon.
- Ridges on coupon in direct contact with Pacific Silvercloth appear more shallow, less pronounced when compared to control coupon – possibly a result of a thicker layer of tarnish on the coupon in contact with Pacific Silvercloth.

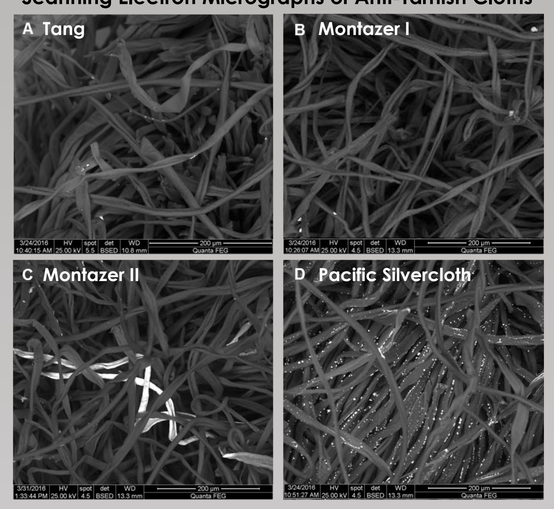
ALTERNATIVE CLOTHS

- Prepared silver-embedded cloths following methods developed for washable, anti-bacterial fabrics.
- Methods utilize cellulose of cotton to reduce silver ions onto the fibers.
- Montazer II and Tang cloths cost approx. \$31/m^2 as compared to Pacific Silvercloth, approx. \$37/m^2 (prices are in Canadian dollars and do not include taxes or shipping).

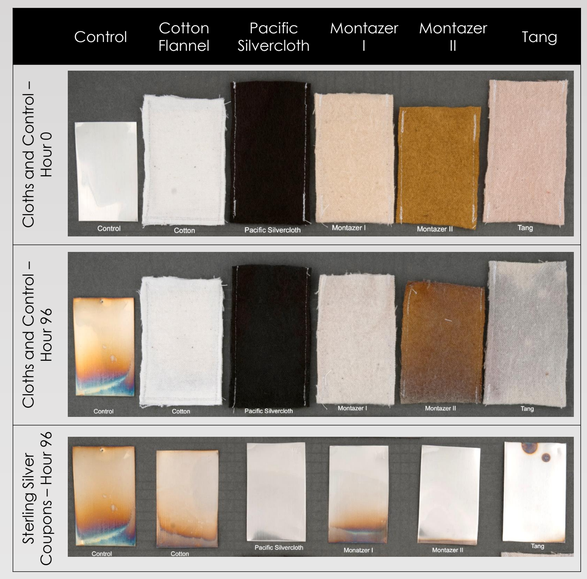
ANTI-TARNISH CLOTHS	
Montazer I	Cotton (1 g/ 20 mL) submerged in solution of 35 ppm Ag_2O + 0.6 mM NH_3 heated to 100°C for 30 min.
Montazer II	Cotton (1 g/ 20 mL) submerged in solution of 400 ppm Ag_2O + 36 mM NH_3 heated to 100 °C for 30 min.
Tang	Cotton (1 g/ 100 mL) submerged in solution of 1mM $AgNO_3$ for 60 hours at room temp. Raised pH to 8 with NaOH after 12 hours.

- Confirmed presence of silver in cloths using SEM-EDS.
- Silver present in Montazer and Tang cloths in smaller quantifies and less dispersed than in Pacific Silvercloth – would likely benefit from higher concentrations of silver in solution and constant mixing .

Scanning Electron Micrographs of Anti-Tarnish Cloths



- Compared anti-tarnish properties of Montazer and Tang cloths to Pacific Silvercloth using a sulfur vapour chamber.
- All 4 anti-tarnish cloths showed reduced to no tarnishing of sterling silver compared to the bare and cotton controls.
- Montazer II and Tang cloths performed better than Montazer I cloth, which contained less silver.
- Montazer II and Tang cloths allowed some tarnishing of sterling silver coupons in areas closest to sulfur vapour source – increasing silver concentration could improve lifetime of cloths.
- Spots of tarnish on Tang coupon due to poor dispersion of silver throughout cloth – could be improved by agitation of solution throughout 60 hour deposition time.
- Pacific Silvercloth not exhausted after 96 hours of sulfur exposure – no tarnish on sterling silver coupon.
- Anti-tarnish cloth alternatives changed colour from yellow to grey as embedded silver became exhausted.
- No noticeable colour change in Pacific Silvercloth.



CONCLUSIONS

- Silvercloth is potentially produced through reaction of silver nitrate and sodium phosphate.
- Preliminary results show Silvercloth contains 5200 ± 800 micrograms of silver per gram of Pacific Silvercloth.
- White, cloudy tarnish on silver appears to result from contact with cellulose and is not specific to Pacific Silvercloth.
- Pacific Silvercloth appears to etch copper-rich areas of sterling silver coupons when in direct contact in high humidity – use of a barrier layer like acid-free tissue and maintenance of low humidity levels is recommended.
- Experiment demonstrates potential application of 'made-in-house' anti-tarnish cloths that change colour to indicate exhaustion.

REFERENCES

ASTM. 2012. Standard Test Method for Extractable Matter in Textiles D2257-98. West Conshohocken, PA: ASTM International.

Gilberg, M., and C. Cook. 1987. Tarnish Inhibitive Papers and Cloths for Silver. IIC-GC Newsletter 12: 14-17.

Lee, L. R. and D. Thickett. 2004. Selection of Materials for the Storage and Display of Museum Objects. *British Museum Occasional Paper* 111.

Montazer, M., Alimohammadi, F., Shamei, A., and M. K. Rahimi. 2012. In situ synthesis of nano silver on cotton using Tollens' reagent. Carbohydrate Polymers 87: 1706–1712.

Selwyn, L. 2004. *Metals and Corrosion: A Handbook for the Conservation Professional.* Ottawa, ON: Canadian Conservation Institute.

Smith, S. M. 2003. Pacific Silvercloth: manufacture, properties, and use in conservation. M.A. diss., Queen's University, Kingston ON.

Tang, B., Kaur, J., Sun, L., and X. Wang. 2013. Multifunctionalization of cotton through in situ green synthesis of silver nanoparticles. Cellulose 20: 3053-3065.

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