Cleaning silver

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The black coating that accumulates on silver over time is silver sulphide, silver oxide, or both. There is sulphur dioxide in the air (on average one cc per cubic metre and more in some industrial areas): not enough for us to smell, but enough to react with silver to form black silver sulphide: Ag_2S.

$$2Ag + SO_2 \rightarrow Ag_2S + O_2$$

The silver pot has been in a cupboard in the house for ten years. The outside has been exposed to air all that time and is black. The black layer is either silver sulphide (Ag_2S), silver oxide (Ag_2O), or both. We assume it's silver sulphide and write reactions with sulphur. The principles are the same if the black is the oxide. To convert silver sulphide to silver we use the well known *baking-soda/aluminium-foil* method.

> *Line the inside of a pot with aluminium foil. Put the blackened item in the pot on the foil. Add a tablespoon of baking soda,* [$NaHCO_3$, sodium bicarbonate], *and cover the silver with hot water (to make the reaction go faster). Wait till the water cools. Take out the pot and wipe it firmly with a soft cloth. Repeat the process with new chemicals if the black layer hasn't been completely removed.*

Hint:

Put the foil over the outside of the container to make it easier to slip inside.

Note: aluminium reacts with oxygen in the air to form aluminium oxide. Unlike calcium metal, which soon becomes a pile of white powder if exposed to air, a thin transparent oxide layer forms on the aluminium and acts like varnish to stop more oxide forming. The aluminium oxide layer is so thin that electric current passes through it.

Why baking soda?

Baking soda doesn't clean silver. It makes the water alkaline with $(OH)^-$ ions and that dissolves the aluminium hydroxide layer that forms on the foil and might stop the metals from making good electrical contact. The bicarbonate effectively cleans the foil.

Silver atoms attract electrons more strongly than aluminium atoms. (Silver is said to be more *electronegative*.) When aluminium makes *electrical contact* with silver an electron current flows from the aluminium to the silver. Sulphur atoms are transferred from association with silver ions (Ag^+) in the existing silver sulphide to aluminium ions (Al^{3+}) in newly forming aluminium sulphide.

The chemical equation for that is …

$$3Ag_2S + 2Al \rightarrow 6Ag + Al_2S_3$$

The reaction that converts Ag_2S to Ag is *electrochemical*: a reaction that involves an electron current. [*The electrochemical reaction that occurs when copper and zinc plates are separated by cloth soaked in common salt solution was used by Volta in 1700 to make the first practical battery.*]

Note: there are more chemical reactions that take place in the hot water, one of which produces a small mount of hydrogen sulphide. You might notice a faint smell of rotten eggs.

Tarnished silver before and after cleaning

The uncleaned silver pot on the left had been on the shelf for the same time as the now clean pot on the right.

Note: *this cleaning method may redistribute silver and should not be used on valuable silver coins*, but it doesn't reduce the weight of silver, like polishing with abrasives to remove silver sulphide.

More possibilities

There are You Tube videos, blogs and accounts in text books that recommend sprinkling the aluminium foil with equal parts of baking soda and common salt (NaCl), and some recommend using only common salt.

Common salt as electrolyte

Both parts of the silver pot below are more black than silver.

Cleaning with salt

> *The inside of the beaker was lined with foil as before and the pot (without the lid) was placed on the foil with a tablespoon of common salt* (NaCl). *The pot was then covered with boiling water as before*.
>
> *When the water had cooled the pot was taken out and washed*.

The pot after treatment with salt, aluminium foil and hot water.

Much of the black layer was converted to silver but a brown patina remained. Repeating the process with sodium chloride and boiling water made little if any improvement.

The partly cleaned pot was treated again with baking soda, new aluminium foil, and boiling water.

The partly cleaned pot after the baking soda treatment.

The baking soda converted the remaining patina to silver metal.

Common salt solution provides a conductive path to allow electron current to flow between the aluminium and silver with the transfer of sulphide ions, but transfer is more compete in sodium bicarbonate solution, probably because the bicarbonate cleans the aluminium as described above.

> Note: black deposits on tarnished silver are likely to contain black silver oxide as well as the sulphide. In this case reactions convert silver oxide to aluminium oxide and hydroxide and the mechanism and result is the same.

To read a patent application for a battery made from aluminium metal, with silver oxide as the positive electrode, in a sodium hydroxide (NaOH) solution see … https://patents.google.com/patent/EP0476916A1/en

Zinc is used as the second electrode in rechargeable silver oxide batteries. Try a web search for “silver oxide batteries”.