In this paper, we report new photoelectric measurements that throw light on the effect of arcing in air on the electron work function (EWF) of contact pastilles made of pure silver [Ag (99.999%)], silver-nickel alloy [Ag-Ni (60/40)], silver-tungsten alloy [Ag-W (50/50)], and silver-tungsten carbide [Ag-WC (50/50)]. The influence of industrial treatment (polishing, mechanical shocks, and electrical arcs in air) of pure metals and silver-metal alloys on their EWF is experimentally investigated. To study the effects of arcing on the EWF, the metallic samples were subjected to electrical arcs in air, at atmospheric pressure, and room temperature, after that, they have been introduced into the vacuum chamber of an experimental ultrahigh vacuum setup for EWF measurements. Fowler's method of isothermal curves was used for the measurement of the EWF by the photoelectric effect. Contacts were mounted in a contactor working repetitively in air (laboratory atmosphere). A cycle of arcing consisted in opening contacts on charging, with production of an electric arc with adjustable duration, and closing a few seconds after arc extinction at zero voltage. When subjected to 500 arcs, the EWF for Ag contacts is $4.50 ± 0.03$ eV at room temperature, while for virgin Ag contacts, it was 4.30 ± 0.03 eV. The increase in the EWF is due to the progressive inclusion of silver oxide in the Ag contact surface during arcing in air. The conditioned (500 arcs) silver--metal alloys studied in this paper exhibit the same electronic emission behavior, namely, arcing in air increases their EWF. We demonstrated that the electromechanical conditioning by successive electrical arcs affects the photo-EWF