



Article: Notes on a Preliminary Investigation into Bronze Powder Deterioration of Albumen Prints

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NOTES ON A PRELIMINARY INVESTIGATION
INTO BRONZE POWDER DETERIORATION
OF ALBUMEN PRINTS

By Barbara Brown

The degradation of albumen photographic prints, in the form of small whitish or yellowish spots on the image, is thought to result from contact with particles of bronze powders used in gilding photographic mounts and album pages. This gilded type of decoration was done from approximately 1850 into the late 1890's. The bronze powders are actually brass - their composition is copper and zinc.

The cause of the faded spots is not understood. A reaction between the printed-out silver image material and the copper and/or zinc components of the powder particles may be at least partly responsible. Jim Reilly has suggested that a reaction of the zinc component, via peroxides, may oxidize the silver metal particle(s) with which it is in contact, thus leaving a silver-deficient or faded spot in the photographic image area.

The goal of this research project is to determine if this deterioration of albumen prints may be caused by a reaction of the copper and/or zinc of the bronze powder with the silver particles constituting the photographic image. Also to be considered is whether the photographic binder medium plays any role in the degradation. If such reactivity is found, it is hoped that it can be determined if such a reaction is autocatalyzed either by the reaction products or by-products.

Three approaches are being taken in the research. First, to analyze the materials used in the gilding; second, to characterize the physical and chemical nature of the spots; third, to attempt to reproduce this deterioration using contemporary materials.

Historically, the term "bronze" is more descriptive of the hue/tone of the powders than their composition, as discussed in an 1877 issue of the British Journal of Photography. It states: "The actual composition of the bronze powder varies according to the color required"¹ The article goes on to give two general formulas used in the production of bronze powders for gilding. One confirms that the alloy involved was actually brass, with the copper provided by verdigris (copper acetate), combined with "impure oxide of zinc" along with flux materials. The other formula is bisulphide of tin.

Because of the ambiguity surrounding the compositions of these powders, we decided to use x-ray fluorescence to determine their elemental composition. Janice Carlson of the Winterthur Analytical Laboratory and I used x-ray fluorescence to analyze the gilding on 7 mounted photographic prints, and the pages of three different photographic albums. The printing and/or decoration on flat surfaces, and the gilding on edges were analyzed. We found all the album pages examined and 50% of the photograph mounts had edges gilded in gold. The gilded printing and/or decoration on the surfaces of the album pages and on 90% of the carte mounts consisted of copper with some zinc (indicating brass). No tin was found in any of these examples. Fourteen different colors of modern bronze gilding powders were also analyzed using x-ray fluorescence. Copper and zinc were the primary constituents.

As part of the second approach, deteriorated spots on historic prints are being examined and documented photomicrographically to gain an idea of their topography. The logical extension of this is scanning electron microscopy. SEM provides high magnification, and in connection with elemental analysis and elemental mapping, we can more fully characterize the nature of these spots. Through the assistance of Mr. Norman Nielsen, retired DuPont metallurgist, the SEM and elemental mapping and elemental analysis will be carried out at the DuPont Experimental Station in Wilmington. Cross-sections of some of the deteriorated spots will be examined to see if there is also a physical change in the binder -- such as "pitting" -- which might confirm interaction of the binder in the deterioration process.

The third part of the research is to attempt to reproduce this form of deterioration using contemporary materials. After the fact, it was learned that this had already been successfully done -- albeit 118 years(!) ago. In 1868, MM. Davanne and Fordos reported: "... a small quantity of bronze powder was strewn over a picture, and its action was then closely watched in a damp atmosphere. After a short time each metallic particle was found to have changed into a black speck, and to have become surrounded by a white halo presenting all the characteristics of the spots which form the subject of the present examination."² Their comments basically describe my experiment. I established a "damp atmosphere" via a humidity chamber containing an RH indicator strip.

A portion of a contemporary albumen print made by duplicating the historic printing technique, and a portion of an exposed and archivally processed silver-gelatin polyfibre photographic paper were used. One of the bronze powders previously analyzed was sprinkled onto the binder surfaces. The samples were placed in the chamber. Every few days the samples were transferred to a fresh chamber to avoid possible mold growth. It has taken one month for any appearance of change -- some possible spots are beginning to be visible to the unaided eye on the albumen samples. In retrospect, the humidity chamber seems to be a slow process as the temperature of the system is ambient room temperature (approximately 65°-68° F). I am considering setting up an accelerated chamber system.

From this experiment, it should also be possible to determine whether or not the binder medium has a role in the reaction (i.e., does the reaction occur preferentially on albumen as opposed to gelatin?). Spots of deterioration will be documented with photomicrographs and analyzed with SEM and elemental mapping and elemental analysis.

Of the three aspects of this research project, the first, analysis of the gilding materials, has been completed. The second, characterization of the nature of the spots, is waiting for SEM/elemental analysis and mapping results on two historic prints. The third, attempt to reproduce this spotted-fading deterioration, has to be documented now that some change is visible.

At present, the only means of preserving albumen printed-out photographs exhibiting this type of deterioration is to remove them from the old mount or album page, if feasible (retaining/recording any pertinent information thereon) thus isolating them from the source of the "bronze"

brass powders. This treatment may be inadequate if the reaction is still occurring. Furthermore, these decorative pages or mounts are often considered an integral part of the object and therefore should be retained intact.

Once more is known about the chemical processes involved in this deterioration of albumen printed-out photographic materials, and whether or not it is on-going even in isolation from the brass particles, then treatments may be derived for the removal of any "auto-catalyzing or -reacting" deterioration products. One possible area to investigate for the removal of deterioration products/treatment of faded spots may be the use of metal-specific or metal-chelating enzymes.

I look forward to bringing you results in the future.

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References:

- 1 Anonymous. "On the Action of Bronze Powder Upon Silver Prints", British Journal of Photography, Vol. 24, NO. 877, 1877, p. 85.
- 2 Davanne, Louis Alphonse; Fordos. "On the Causes of Deterioration of Prints Mounted on Cardboard with Gilt Borders", Photographic Journal, Vol. 13, No. 192, 1868, p.33.

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