doi:10.1017/S1431927611009883
Microsc. Microanal. 17 (Suppl 2), 2011

Microstructure of Woolen Fiber Dyed by $PbCrO_4$ Yellow Dyeing Technique Imported into Japan in the Middle of the 19th Century

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A cotton fabric called *Touzan*, having a vertically striped pattern, was imported into Japan from Southeast Asian countries during the 15-19th centuries. The author found that the chrome-yellow dyeing technique was used for the yellow thread in the *Touzan* fabric imported in the late 19th century [1]. It is thought that the conventional plant-based yellow dye for the thread in *Touzan* fabric was replaced with artificial dye, such as chrome-yellow, developed in Europe. Then, the dyeing technique was brought into Japan, perhaps in the middle of the 19th century, and was utilized to make the cotton fabric called domestic-*Touzan*.

Nanometer-size chrome-yellow compounds were observed in the cotton fiber and the dyeing mechanism of the mineral dyestuff, such as chrome-yellow, was clarified [2]-[4]. The crystallized and amorphous regions of cotton fiber also could be analyzed by precipitate decoration.

Since an animal protein fiber such as wool has a different internal structure from cotton, it is thought that an interesting microstructure and a new observation technique of the internal structure of protein fiber can be obtained. The nanometer-size precipitation behavior in wool and the protein fiber structure of wool observed by precipitate decoration are presented in the meeting.

Wool thread specimens in accordance with Japanese Industrial Standard L 0803 were dyed with chrome-yellow. The dyeing process is as follows. (1) Wool threads are immersed in lead acetate ($Pb(CH_3COO)_2$) aqueous solution for 50 min and then rinsed in water. (2) The threads are next immersed in potassium dichromate ($K_2Cr_2O_7$) aqueous solution for 20 min and then rinsed in water. (3) The threads are then immersed in lead acetate aqueous solution again. The well-known reaction for forming $PbCrO_4$ is $2Pb(CH_3COO)_2 + K_2Cr_2O_7 + H_2O \rightarrow 2PbCrO_4 + 2CH_3COOK + 2CH_3COOH$. Namely, when potassium dichromate is added to lead acetate, lead chromate is formed as a yellow precipitate.

The color of the fabric is measured with a spectrophotometer, and the microstructures are observed with a scanning electron microscope (SEM). To observe the distribution of nanometer-sized compounds in the fiber, the cross-sectional surface of the fiber is flattened by ion milling. The composition and crystal structure are analyzed using energy-dispersive X-ray spectra (EDS) and X-ray diffraction (XRD). The nanostructure of the dyed fiber is observed with a transmission electron microscope (TEM). A thin film for observing the nanostructures is prepared by the focused ion beam method.

The main absorption edges are 538 nm (2.3 eV) for chrome-yellow-dyed wool threads. The wool thread surface and cuticles covered by many particles 1-2 μm in length are observed by SEM. Chromium and lead species are detected from the surface of the wool fiber in the EDS. Peaks of monoclinic $PbCrO_4$ [JPCDS card No. 08-0209], orthorhombic $PbCrO_4$ [JCPDS card No. 50-2241] and very weak peaks of wool are detected by XRD analysis of the chrome-yellow dyed-wool thread.

The distributions of sulfur, lead and chromium in the fibers were examined by EDS. Elemental mappings and a SEM image of the cross sections of the fibers are shown in Fig. 1 and Fig. 2. Sulfur, lead and chromium are almost uniformly distributed throughout the fibers for both imported and Japanese *Touzan* specimens. These elements are the components of chrome yellow. There were observable differences in the two contrasts that divide the middle of the wool cross

section. It is thought that the two different textures correspond to the ortho-cortex and para-cortex of the wool fiber.

Precipitates are observed in the cortex, indicating that there is some macrofibril structure. Pb-Cr-O group compounds were distributed almost circularly in the cotton fiber cross section. The distribution of precipitates in the wool fiber is different from that in the cotton fiber, since the wool structure is difference from the cotton structure. This result indicates that the decoration method of precipitation is useful for elucidating the structure of various fibers. To clarify the state of existence of the dyestuff elements in the fiber, the chrome-yellow-dyed wool fiber was observed with a TEM. A transmission electron micrograph of the yellow fiber is shown in Fig. 3. The crystal compound $PbCrO_4$ precipitates on the wool fiber surface; the length and width of the crystals are 0.2-1.2 μm and 0.05-0.4 nm, respectively. Chromium, lead and sulfur are detected from the inside of the fiber. Referential precipitation is observed in the fiber, and most of the precipitates align along a specific place in the fiber. The precipitate distribution shows a correlation between the precipitation phenomenon and the wool fiber structure, and also reveals the microstructures in the wool fiber. Although the precipitates on the fiber surface are crystalline, nanometer-size precipitates in the fiber are amorphous.

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[2] N. Sugioka and M. Kitada: J. Japan Inst. Materials 73 (2009) 238-243
[3] N. Sugioka and M. Kitada: J. Japan Inst. Materials 73 (2009) 462-468
[4] N. Sugioka and M. Kitada: J. Japan Inst. Materials 74 (2010) 242-249

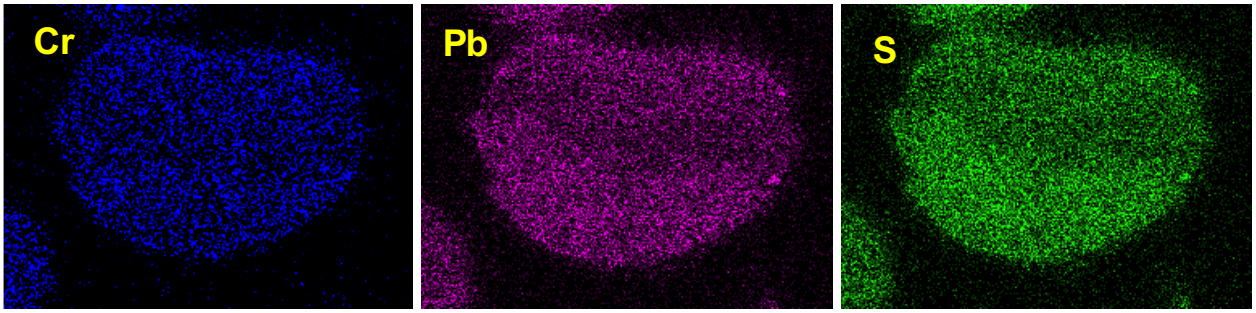

Fig. 1 Cross-sectional elemental mapping of wool fiber dyed with lead chromate solution.

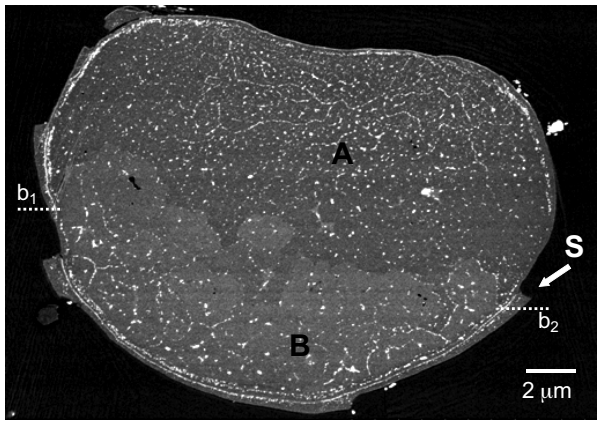

Fig. 2 Cross-sectional SEM image of wool fiber dyed with lead chromate solution. A and B indicate paracortex and orthocortex; the dotted lines indicates the boundaries between them. Arrow S indicates the scale of wool fiber.

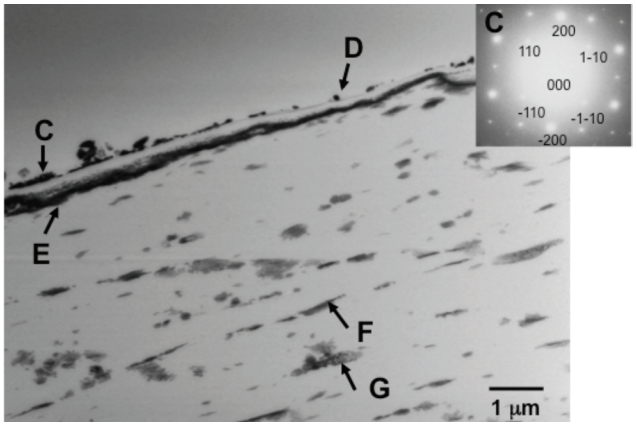

Fig. 3 Transmission electron micrograph of lead-chromate-dyed wool fiber and electron diffraction pattern from precipitate C. Arrows C-G indicate precipitates.

https://doi.org/10.1017/S1431927611009883 Published online by Cambridge University Press