

# Characterization of Nanoscale Wool Particles

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**ABSTRACT:** Nanoscale wool particles were prepared from wool fibers by a special pretreatment with the aid of specially designed machinery and techniques. Scanning electron micrographs showed that the particle sizes of wool powders produced from wool fibers approximately 8–20  $\mu\text{m}$  in diameter decreased from a microscale to a nanoscale after three stages of pulverization, which were further confirmed with a laser particle size analyzer. Fourier transmission infrared analysis showed that there were no substantial changes in the chemical structure of the wool after the pulverization processes. The

wool powders after the second and third pulverizations slightly differed from that of the wool fiber and the particles after the first pulverization, with greater amounts of the secondary amine groups, amide groups, C=S stretching vibrations, and O–H bonds. X-ray diffraction analysis showed that the crystallinity of the wool powders decreased when the particle sizes decreased, particularly at nanoscales. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 803–808, 2007

**Key words:** nanotechnology; wool particles; FTIR; XRD

## INTRODUCTION

Hitherto, natural fibers have been very important and widely used materials in the textile industry because of their unique excellent properties. However, because of the limitations and requirements at the stage of spinning, it is sometimes difficult to spin too short or too weak fibers into yarns, and these fibers may then be disposed during the spinning process. There are many discarded garments all over the world. The excellent intrinsic properties of these discarded fibers could create great market potential for the textile industry if they were to be reused.<sup>1</sup>

Wool is the fiber obtained from the fleece of sheep. It is a natural, multicellular staple fiber and is composed of proteins and organic substances with the composition of carbon, hydrogen, oxygen, nitrogen, and sulfur.<sup>2</sup> The length of wool is dependent on the breed of sheep and the growing time of the fiber. In general, the fiber length ranges from 20 to 300 mm, with shorter fibers usually being finer and longer fibers usually being coarser. The diameter of wool fibers ranges from 8 to 70  $\mu\text{m}$ . The width of Merino fleece fibers is usually 15–17  $\mu\text{m}$ .<sup>3</sup>

Nowadays, in addition to applications in clothing, natural animal fibers, especially wool fibers, have

gained a great deal of attention because of their great potential and use as multifunctional materials in various fields, such as biomedical fields. As a result, many researchers, especially in Japan, have tried to develop new application areas for those fibers because of the application of their excellent intrinsic properties. For example, Yamada et al.<sup>4</sup> proposed a process for the solubilization of animal hair. They mentioned that animal hair has been used as a trapping agent for heavy metals, an additive for cosmetics and food, a hair tonic, and an improver for clothing. They pointed out that animal hair is expected to be more extensively used as additives for cosmetics and foods, blending components for various industrial treating agents or materials, medical materials, industrial materials, blending ingredients for foods, and so forth. Miyamoto and Inagaki<sup>5</sup> also conducted research into the preparation of wool powders by an explosive puffing treatment. Xu et al.<sup>6</sup> suggested a method for generating ultrafine wool powder by milling and analyzed the thermal properties of the powder. Li and Hu<sup>1</sup> reported the development of a technique for pulverizing natural organic substances such as wool, cotton, and silk fibers into nanoscale, fibrous materials. Li and Xu<sup>7</sup> also demonstrated the invention of an apparatus for preparing fine powders from wool and silk.

In these studies, the main focus has been on techniques to prepare superfine and/or nanoscale powders from wool fibers. In this article, we report the analysis of the structural characteristics of wool powders with particle sizes ranging from a microscale to a nanoscale during different stages of pulverization by employing a number of techniques, including scanning electron microscopy (SEM), laser particle analysis, Fourier

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transmission infrared (FTIR), and X-ray diffraction (XRD).

## EXPERIMENTAL

### Preparation of the wool powders

In this research, wool fibers were pulverized into a nanoscale powder step by step. The steps for the pulverization process are described briefly next.

The wool fibers were first weakened by being dipped into a 15–30% hydrogen peroxide solution at room temperature for about 5 min, and this was followed by washing with distilled water. The excess water inside the fibers was removed by the drying and baking of the wool fibers at 130°C for 1 h. The weakening of the wool fiber by the hydrogen peroxide was due to the progressive oxidation of the disulfide bonds. As a result, the further treatment for the preparation of the nanowool powder was facilitated by the hydrogen peroxide treatment.

After clearing and drying, the weakened wool fiber was cut into pieces 1–2 cm long and then crushed into small piece by a mechanical rotating crusher with a particle length of around 300  $\mu\text{m}$ . The obtained powder was called the first pulverized wool powder.

The first pulverized wool powder (20 g) was then mixed with 800 mL of water and pulverized with an ultrasonic crusher (JY-99 II D, Ningbo Scientz Technology Co., Ltd., Ningbo City, China) for 40 min. After this pulverization step, the majority of the wool particles in the suspension were smaller than 7  $\mu\text{m}$ . The powder obtained after this step was microscale in size and was called the second pulverized wool powder.

Then, the second pulverized wool power suspension was filtered to remove large, uncrushed particles. After crushing and filtration, the filtrate suspension that was obtained was pulverized into a nanoscale wool suspension by an ultraturray machine at first and then by a nanocolliding machine (model NT1500/5, Beijing Nanomizer Technology Research Institute, Beijing, China) under a pressure of 1000 kgf/cm<sup>2</sup> at a speed of 300 rpm for final pulverization. After this process, the particles were smaller than 100 nm in diameter. The powder obtained after these steps was nanoscale in size and was called the third pulverized wool powder.<sup>1</sup>

### Characterization of the superfine wool powders

This research studied the morphology, particle size distribution, chemical structure, and crystallinity of the first, second, and third pulverized wool powders by means of SEM, particle size analysis, FTIR spectroscopy, and XRD analysis, respectively.

The morphology of the pulverized wool powders was examined with SEM analysis, which was carried

out with a JSM 6335F field emission scanning electron microscope (JEOL Ltd, Tokyo, Japan) after gold coating.

The particle size distributions of the first, second, and third pulverized wool powders were analyzed with a Beckman Coulter LS 13320 particle size analyzer (Fullerton, USA), which was designed from conception to be fully compliant with ISO/DIN13320-1 ("Particle Size Analysis—Laser Scattering Methods—Part 1: General Principles").

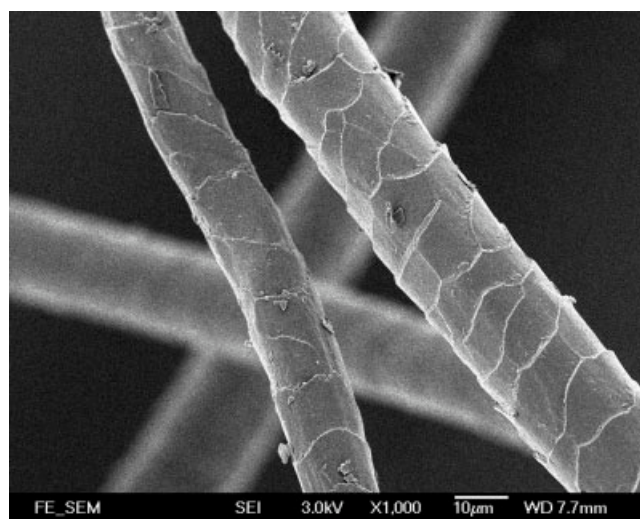
To study whether there were any chemical changes in the wool after pulverization, the FTIR spectra of the first, second, and third pulverized wool powders were studied. In this research, the KBr disc technique was used for the preparation of the pulverized wool powders for FTIR analysis. This method consisted of mixing the finely divided pulverized wool powder samples (0.004 g) with 0.4 g of powdered potassium bromide. The discs were formed in a die under a very high pressure and then were analyzed with a Perkin-Elmer 2000 FTIR spectroscopy system (Wellesley, USA).

The crystallinity of the pulverized powders was determined by the XRD technique. The XRD experiments were conducted on the pulverized wool powders with a Philips Analytical PW3710 based X-ray diffractometer (Almolo, The Netherlands) with a copper-tube anode source at 40 kV and 35 mA. A 0.1-mm-pinhole collimator was employed. Scattering XRD data were recorded with an XRD evaluation program (Advanced X-Ray Solutions Diffract Plus Release 2000 Eva, version 6.0, Bruker, Madison, USA).

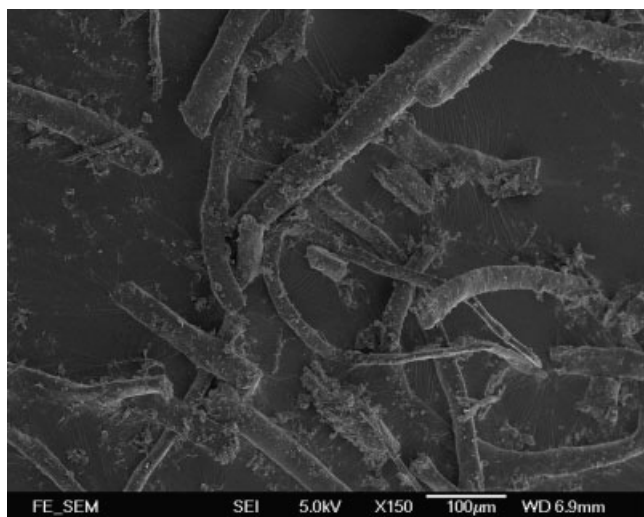
## RESULTS AND DISCUSSION

### SEM

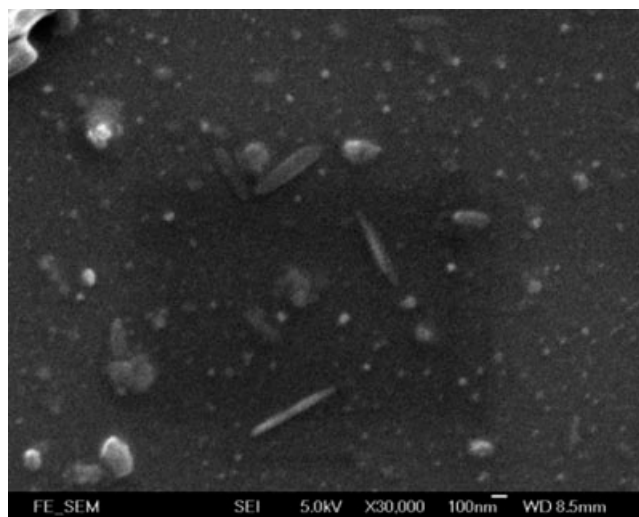
Figure 1 shows that the length of the original wool fibers was on a millimeter scale, and their diameter



**Figure 1** SEM image of wool fibers (original magnification = 1000 $\times$ ). The diameter of the fibers was 8–20  $\mu\text{m}$ .

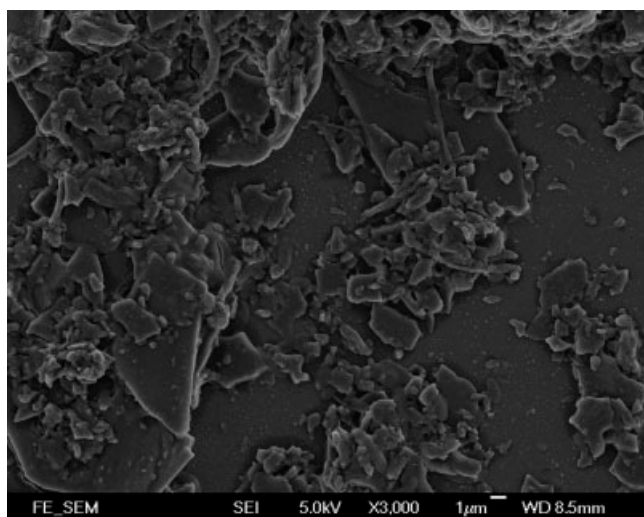


**Figure 2** SEM image of the first pulverized wool powder (original magnification = 150 $\times$ ).



**Figure 4** SEM image of the third pulverized wool powder (original magnification = 30,000 $\times$ ).

was around 8–20  $\mu\text{m}$ . The surface of the wool fibers consisted of a fine network of small, overlapping scales. Figure 2 shows that after the first pulverization process, the fibers were smashed into a combination of a large, rodlike powder of around 300  $\mu\text{m}$  and a large amount of a superfine powder of less than 10  $\mu\text{m}$ . The scales of the wool fibers were also removed after the first pulverization process. Figure 3 shows that the second pulverized wool powder (ca. 0.1–7  $\mu\text{m}$ ) was obtained after the second pulverization process. Most of the second pulverized wool powder was in a sheet form. Figure 4 shows that most of the third pulverized wool powder was a nanoscale spherical powder, whereas some was rodlike in shape.

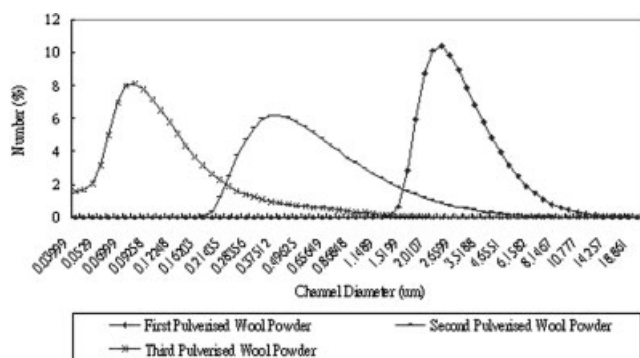


**Figure 3** SEM image of the second pulverized wool powder (original magnification = 3000 $\times$ ).

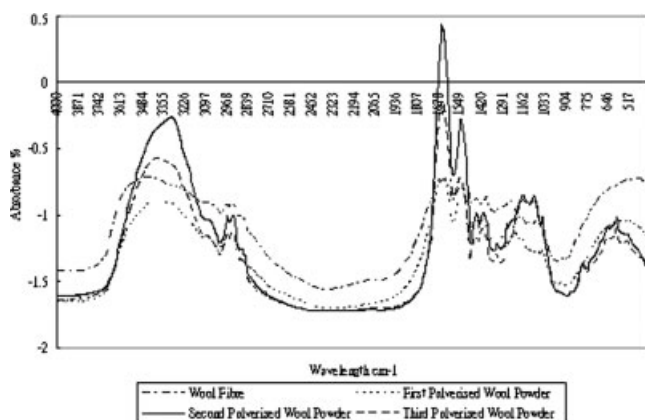
#### Particle size analysis with a laser particle size analyzer

The aforementioned SEM images showed that after the second and third pulverization processes, microscale and nanoscale wool powders were generated, respectively. These SEM pictures only visually showed the images of wool powders located in a specific area and did not provide a quantitative analysis for the actual particle size distribution of the powders. As a result, the particle size distributions of the first, second, and third pulverized wool powders were analyzed with the Beckman Coulter LS 13320 particle size analyzer.

Figure 5 shows that the particle size of the first and second pulverized wool powders ranged from approximately 1 to 15  $\mu\text{m}$  and from approximately 0.15 to 7  $\mu\text{m}$ , respectively. The powders with a diameter of less than 0.1  $\mu\text{m}$  were classified as nanoscale wool powders. This confirmed that most of the third pulverized wool powder was nanoscale.



**Figure 5** Particle size distribution of the first, second, and third pulverized wool powders.



**Figure 6** FTIR absorption spectra of the first, second, and third pulverized wool powders.

The resulting particle size distributions of the pulverized wool powders needed to be confirmed by observation through SEM images to determine the morphology of the wool particles. The laser diffraction technique of the LS 13320 particle size analyzer is based on the phenomenon that particles scatter light in all directions with an intensity pattern that depends on the particle size. All these instruments assume that the particles are spherical. For nonspherical particles, an equivalent-sphere size distribution is obtained because the technology makes the assumption of spherical particles in its optical model. Therefore, the resulting size distribution may differ from those obtained by methods based on other physical principles, such as sedimentation and sieving. This deconvolution is found according to the Fraunhofer theory of light scattering.<sup>8</sup> Xu and Di Guida<sup>9</sup> pointed out that for nonspherical particles for which the diameters are ill defined and theoretical models of scattering patterns are seldom available, the results obtained from the application of any spherical model will certainly have unexpected bias or error.

In practice, most people neglect the difference between the real shapes of particles and the model and customarily take the reported mean values and size distributions for granted without realizing that these are only apparent sizes and actually are not equivalent sizes. In certain extreme cases, the results obtained by the application of the spherical model to nonspherical particles will be very different from the truth.

The SEM image of the first pulverized wool powders in Figure 2 shows that there were particles around 300  $\mu\text{m}$  long. The particle size distribution in Figure 5, however, can hardly identify such particles. This difference can be attributed to a number of potential causes: (1) the powders in a specific area of the SEM images were randomly selected, (2) the particles were assumed to be spherical in the particle size analyzer, and (3) the particle size analysis was based on the counting of the number percentage of the pow-

ders. The first pulverized wool powder might have consisted of only a limited number of large particles (300  $\mu\text{m}$ ) in such an amount that was negligible for counting the number percentage as most of the first pulverized wool powder was around 1–15  $\mu\text{m}$ .

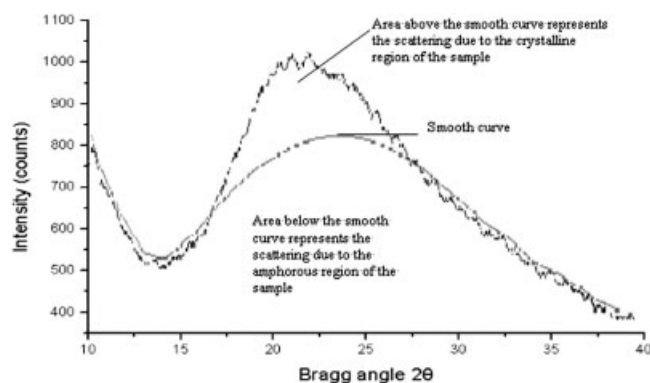
The SEM image of the third pulverized wool powder shows that most of the particles were almost spherical, and the diameters were less than 100 nm; this was consistent with and validated the measurement results from the laser particle size analyzer.

### FTIR spectroscopy analysis

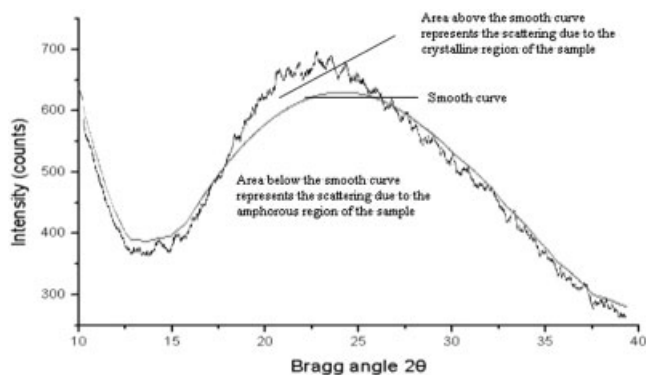
To study whether there were any chemical changes in the wool after pulverization, the FTIR spectra of the first, second, and third pulverized wool powders were studied. The FTIR checked the functional groups of the wool fiber. Those functional groups, as indicated in this article, are the representative functional groups of the wool fiber. The FTIR spectra of the pulverized wool powders shown in Figure 6 confirmed that there were no very great changes in the chemical structure of wool after the pulverization processes. However, the FTIR spectra of the wool fiber and the first pulverized wool powder only slightly differed from those of the second and third pulverized wool powders within the ranges of 1000–1800 and 3230–3670  $\text{cm}^{-1}$ .

Within the 1000–1800  $\text{cm}^{-1}$  range, the FTIR spectra illustrate that the second and third pulverized wool powders had a stronger absorbance band within 1490–1580  $\text{cm}^{-1}$  and a stronger peak near 1655  $\text{cm}^{-1}$  than the wool fiber and the first pulverized wool powders, and this might be due to the greater number of secondary amine groups and amide groups present in the second and third pulverized wool powders.

The second and third pulverized wool powder also had higher absorption in the region of 1030–1230  $\text{cm}^{-1}$ , which might be due to the greater amount of C=S stretching vibration of the second and third pulverized wool powders in comparison with the



**Figure 7** XRD pattern of the first pulverized wool powder with  $2\theta$  ranging from 10 to 40°.

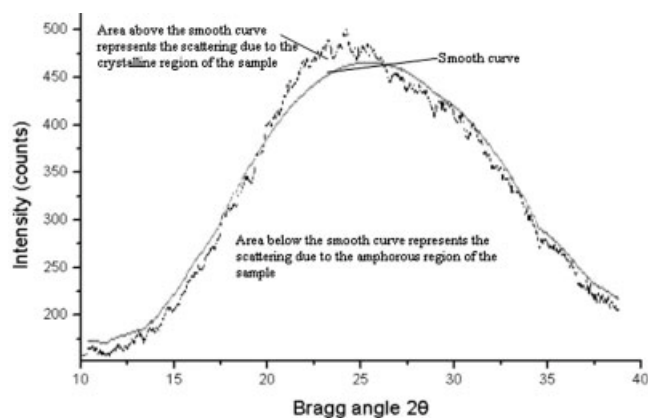


**Figure 8** XRD pattern of the second pulverized wool powder with  $2\theta$  ranging from 10 to  $40^\circ$ .

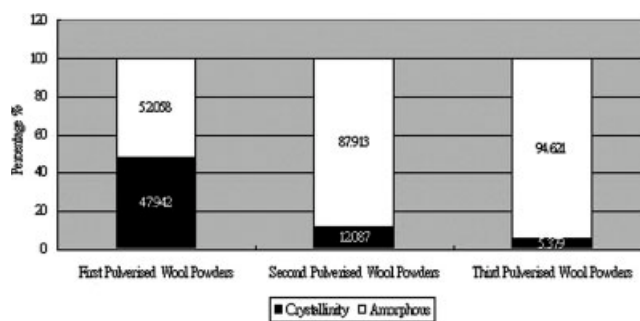
wool fiber and the first pulverized wool powder. The stronger absorbance band within the region of  $3230\text{--}3670\text{ cm}^{-1}$  of the second and third pulverized wool powder in comparison with the wool fiber and the first pulverized wool powder might be the result of the greater number of O—H bonds in the second and third pulverized wool versus the wool fiber and the first pulverized wool powder.<sup>10</sup>

### XRD analysis

In this study, XRD analysis was used for assessing the physical changes in the wool. The XRD analysis determined the crystallinity of the wool fiber and was used to indicate the dramatic change in the crystallinity of the wool fiber. The XRD evaluation program (Advanced X-Ray Solutions Diffract Plus Release 2000 Eva, version 6.0, Bruker) allowed convenient data transfer and analysis. The method for determining the crystallinity percentage was based on the estimation ratio of the crystalline material to the amorphous material in the sample. It was obtained from modified XRD intensity profiles by the drawing of a smooth curve through the minima of the principal dif-



**Figure 9** XRD pattern of the third pulverized wool powder with  $2\theta$  ranging from 10 to  $40^\circ$ .



**Figure 10** Crystallinity and amorphous percentages of the first, second, and third pulverized wool powders.

fraction effects and the comparison of the areas below and above the curve over an angular range of  $2\theta = 10\text{--}40^\circ$ . The smoothing curve was generated with the background function of the program Eva.

The XRD patterns of the samples were divided into crystalline and amorphous regions with a smooth curve, as shown in Figure 7. The area above the curve corresponded to the scattering due to the crystalline region of the sample, whereas the area below the curve responded to the amorphous region.

Figures 7–9 show the XRD intensity of the pulverized wool powders with  $2\theta$  ranging from 10 to  $40^\circ$ . The area above the smooth curve represents the scattering due to the crystalline region of the samples. The area above the smooth curve decreased with the smaller particle size of the powders, and this meant that the crystallinity of the powders decreased with their particle size too.

Figure 10 is a graph presenting the crystallinity and amorphous percentages of the powders, which were determined by a comparison of the areas above and below the smooth curve with the aid of the XRD evaluation program. The results showed that the crystallinity percentage of the wool powders decreased from 47.942% for the first pulverized wool powder to 12.087 and 5.379% for the second and third pulverized wool powders, respectively.

### CONCLUSIONS

Particle size analysis and SEM images of the pulverized wool powders showed that the particle sizes of the wool powders decreased from a microscale to a nanoscale with the progress of the three-stage pulverization. The FTIR spectra of the pulverized wool powders illustrated that there were no substantial changes in the chemical structure of wool after the pulverization processes. The differences in the FTIR curves showed slight changes in the chemical structure between the samples, indicating that the second and third pulverized wool powders contained more secondary amine groups, amide groups, C=S stretching vibrations, and O—H bonds than the wool fiber and

the first pulverized wool powders. The XRD analysis showed that the crystallinity of the pulverized wool powders decreased with decreasing particle size.

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