

ORIGINAL ARTICLES

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Improvement of fiberboard made from acetylated fibers by ozonation I: effect of ozonation on mechanical properties

Received: June 21, 1999 / Accepted: February 23, 2000

Abstract Acetylated fibers with a 24.8% weight gain by acetylation were ozonated with 0%–2.0% ozone on fibers. Fiberboards were then made from these treated fibers. The internal bond and bending strength of the acetylated fiberboards increased drastically with increasing ozone charge up to 0.5%–1.0%, whereas the thickness swelling of the fiberboards decreased. Ozone selectively cleaves the aromatic rings of hydrophobic lignin and introduces a hydrophilic carboxyl group into lignin. Thus, the wettability and thermoplasticity of acetylated fibers increased, and this structural modification improved the interfiber contact. Internal bond and bending strength increased as a result. In addition, steep density profiles were formed by the ozonation, resulting in high bending strength. The high compaction ratio accelerated the effect of ozonation. The optimum ozone charges for improving mechanical properties were 0.5%–1.0%.

Key words Fiberboard · Ozone · Acetylation · Wettability · Thermoplasticity

Introduction

One of the disadvantages of wood-based composites is dimensional change when the composites are exposed to periodic changes in atmospheric humidity. To overcome this dimensional change, composites were made from acetylated wood elements,[1–3] but the mechanical properties of acetylated composites declined.[4] One of the reasons is low wettability for aqueous adhesives, which results in poor bonding strength.[2,4] In this study, we have tried to increase the wettability of acetylated wood element by ozonation[5,6] while maintaining the dimensional stability.

The utilization of ozone improved the mechanical properties of the pulp[7] in the studies on bleaching of high yield pulp. As to composites, Chow ozonated the bark of Douglas fir and western red cedar to make binderless board.[8] Takata et al. reported on the improvement of the mechanical properties of the fiberboards made from ozonated waste paper.[5,9]

The reaction of ozone with wood components mainly is attributed to lignin.[9] The primary and main attack by ozone increases the carboxyl groups in lignin and reduces the aromatic character.[7] The increased carboxyl groups help activate the fiber surface and improve bonding ability.[9] In this study, hydrophobic acetylated fibers were ozonated to add hydrophilicity to the lignin; thereby, the wettability of acetylated fibers increased while hydrophobic acetylated cellulose was maintained. The effect of ozonation was then evaluated based on the mechanical properties of the novel fiberboards made from ozonated fibers after acetylation.

Experimental

Contact angle

Solid wood of Hinoki (*Chamaecyparis obtusa* Endl) was sliced into samples with a radial face of 8.5 cm (axial) × 2.5 cm (radial) × 0.2 mm (tangential) for measuring the contact angle. The test pieces were subjected to extraction by ethyl alcohol and benzene (v/v 1:2) for 6 h, and then acetylated by liquid-phase acetic anhydride heated to 120°C for 6 h. The mean weight gain was 18.9%. Then the acetylated and unacetylated wood was ozonated.[5,9] The ozone charges were 0%, 0.25%, and 0.5% (based on

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Part of this report was presented at the 49th Annual Meeting of the Japan Wood Research Society, Tokyo, April 1999

the oven-dried weight of the wood). The contact angles of water-drop about 35 s later were measured by a face contact-angle meter (Kyowa Kaimenkagaku) in the axial direction, and 50 water-drops were measured.

Raw material of fiberboard

Wood fibers from yellow cedar (*Chamaecyparis nootkatensis (D. Don) Spach*) having an air-dried density of 0.51 g/cm^3 were used as raw material.[10] Acetylated fibers were prepared by vapor-phase acetic anhydride, and the weight gain was 24.8%.[3] Acetylated and unacetylated fibers were ozonated[5,9]; the ozone charges were 0%, 0.25%, 0.5%, 1.0%, and 2.0% (based on the oven-dried weight of the fibers).

Manufacture of fiberboard

Acetylated and unacetylated fiberboards were made from ozonated fibers after acetylation or without acetylation. The adhesive was melamine formaldehyde resin, (U-816; Mitsui Chemical Co.) of which the solid content was 65%. Ammonium chloride was added to the resin (1% by weight) as hardener. A 10% water solution of ammonium chloride was prepared, and it was added to the adhesive. The target resin content was 15% (based on the oven-dried weight of the fiber). The moisture contents of acetylated and unacetylated fibers before spraying adhesive were 2.3% and 6.5%, respectively. The mat moisture content of unacetylated fibers after spraying was about 18%. Water was added to the adhesive for acetylated fibers to make the mat moisture content same as unacetylated fibers.

The adhesive solution was sprayed onto the agitating fibers, and a fiber mat was formed. The mat was pressed by the hot press (HP-200T, Nisshinkagaku) at 180°C for 5 min. Two distance bars 10 mm height were used. The dimension of the boards was 18 × 22 × 1 cm. The target board densities were 0.5 g/cm^3 (low-density board) and 0.7 g/cm^3 (medium-density board). Two boards were made under each experimental condition.

Property testing

Test pieces were conditioned under 20°C and 65% relative humidity for about 1 week. Modulus of rupture (MOR), internal bond strength (IB), and thickness swelling (TS) were measured according to JIS A 5905 1994. Six replications for each series were performed.

Density profiles were obtained by sanding 0.5–1.0 mm from the surface of a nondestructive portion of bending test pieces. The face and core in the density profile were defined (Fig. 1): The thickness of the face was defined as 0.5–1.5 mm depth from the surface; in other words, the first 0.5 mm of thickness from the surface was excluded.[11] The core was defined as the innermost 0.5 mm of the boards.

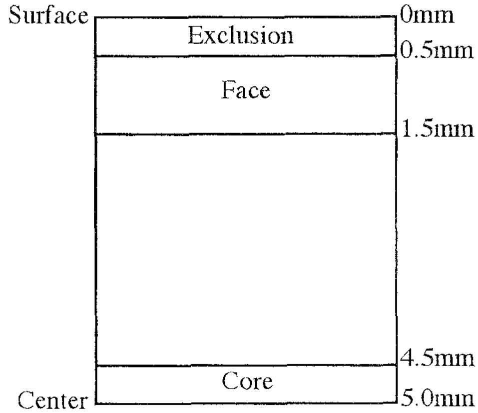

Fig. 1. Face and core dimensions

Table 1. Contact angle of acetylated and unacetylated wood with ozonation

Wood	Contact angle, by % ozone change		
	0	0.25	0.50
Unacetylated	24 (4.1)	23 (4.4)	–
Acetylated	31 (4.8)	30 (3.4)	25 (3.9)

It was impossible to measure the contact angle of unacetylated wood at 0.5% ozone charge owing to the low contact angle
The numbers in parentheses indicate standard deviations

Results and discussion

Contact angle

The contact angle was studied to determine the effect of ozonation on wettability.[6] The results in Table 1 show the contact angle. The contact angle of acetylated wood was higher than that of unacetylated wood, and it decreased with increasing ozone charge. The contact angle of unacetylated wood at 0.5% ozone charge was too low to be measured. Thus, it was shown that the wettability of aqueous adhesives was improved by ozonation.

Density profile

Figure 2 shows the density profiles, which are depicted by each density in the depth divided by the mean board density, and this is defined as the "relative density."[12] Rowell et al. reported that an acetylated board had a uniform density profile.[1] However, the steep density profiles of acetylated medium-density boards were formed by ozonation in this study. Ozone cleaves the aromatic rings of lignin,[7,9,13] presumably increasing the thermoplasticity of acetylated fibers. High heat and vapor plasticize them, and they are then compressed easily from the face to the core gradually during hot pressing.

The steep density profiles of acetylated low-density boards were not formed by ozonation. Fibers are not compressed sufficiently for effective contact among fibers

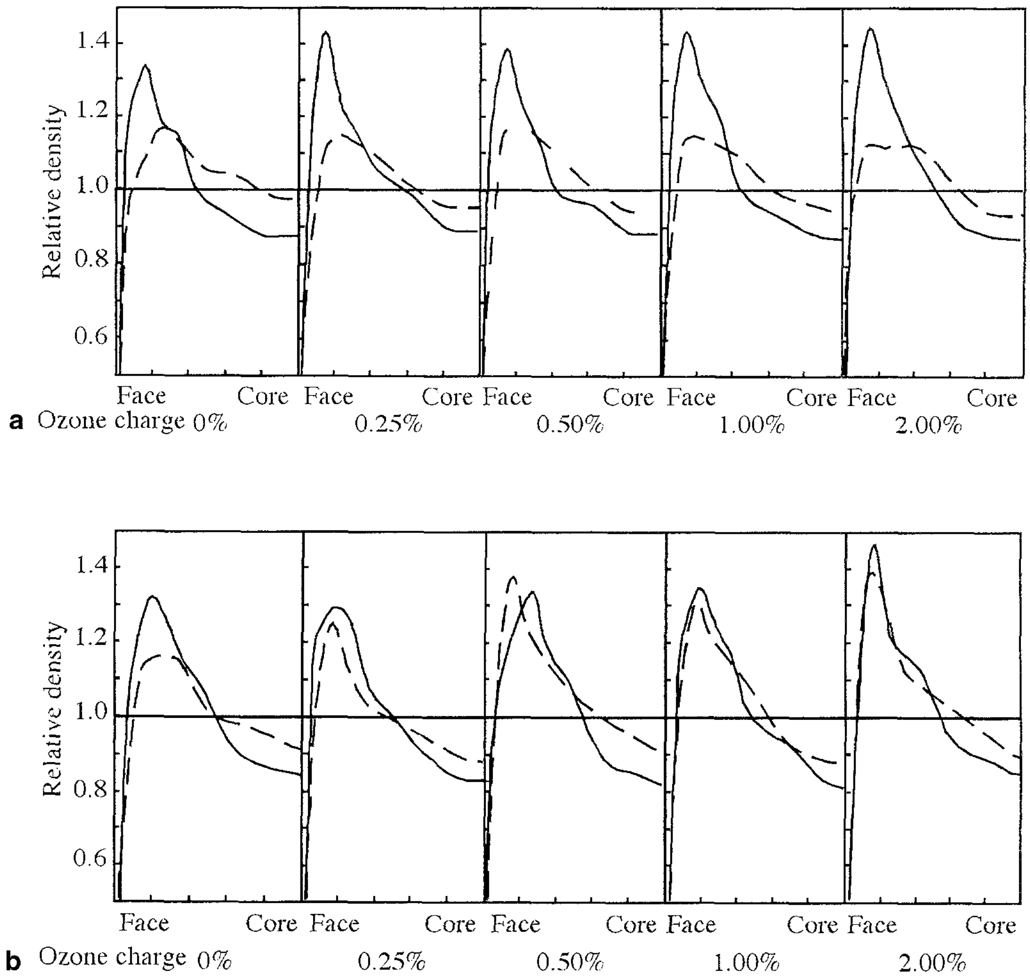

Fig. 2. Relative density profiles of fiberboards. Relative density was each density in the depth divided by the mean board density. **a** Low-density board, 0.5 g/cm^3 target board density. **b** Medium-density board, 0.7 g/cm^3 target board density. *Solid lines*, unacetylated boards; *dashed lines*, acetylated boards

Table 2. Core density and face density under each ozone charge

Board[a]	Core density (g/cm^3), by % ozone charge					Face density (g/cm^3), by % ozone charge				
	0	0.25	0.50	1.00	2.00	0	0.25	0.50	1.00	2.00
Unacetylated low-density	0.48	0.48	0.51	0.48	0.47	0.67	0.68	0.71	0.71	0.71
Acetylated low-density	0.50	0.51	0.53	0.51	0.51	0.57	0.59	0.64	0.61	0.60
Unacetylated medium-density	0.61	0.61	0.61	0.60	0.58	0.91	0.92	0.90	0.93	0.90
Acetylated medium-density	0.62	0.65	0.64	0.61	0.65	0.75	0.83	0.90	0.84	0.93

Refer to Fig. 1 for the explanation of core and face

[a] Low-density and medium-density are 0.5 g/cm^3 and 0.7 g/cm^3 target board density, respectively

presumably due to a low compaction ratio (mean board density/raw material density). A high compaction ratio may improve the contact among fibers, and it is expected to accelerate the effect of ozonation.

Internal bond strength

Increasing the wettability and thermoplasticity may improve interfiber contact, which is confirmed by the IB shown in Fig. 3. The IB of acetylated boards increased drastically at 0.25% ozone charge. It was obvious that ozonation improved the interfiber contact, resulting in high IB. Without ozonation, the IB of acetylated board was much lower than that of unacetylated board, probably owing to low interfiber contact.

In general, IB is related to the core density[14] as shown in Table 2. The IB of almost all boards increased drastically with increasing ozone charge (Fig. 3), although core density did not increase drastically. When unacetylated low-density boards and unacetylated medium-density boards are compared, the IB of the former decreased at high ozone charges, but the IB of the latter increased; both core densities decreased. It can be concluded that a high compaction ratio accelerates the effect of ozonation.

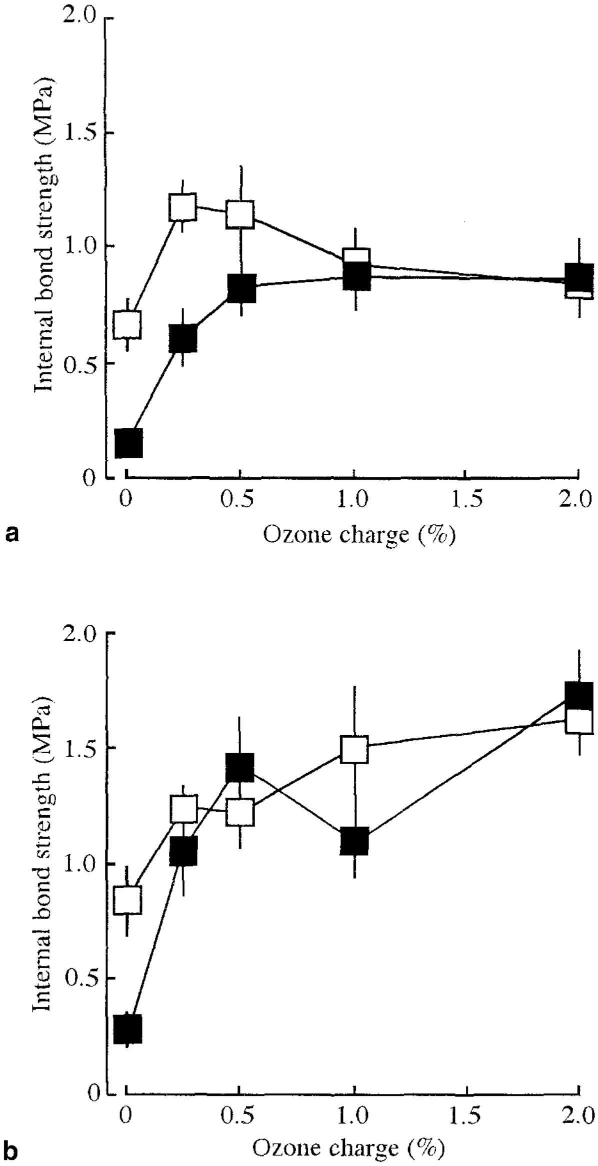

Fig. 3. Relations between ozone charge and internal bond strength. **a** Low-density board, 0.5 g/cm^3 target board density. **b** Medium-density board, 0.7 g/cm^3 target board density. *Open squares*, unacetylated boards; *filled squares*, acetylated boards. *Vertical lines* denote standard deviations

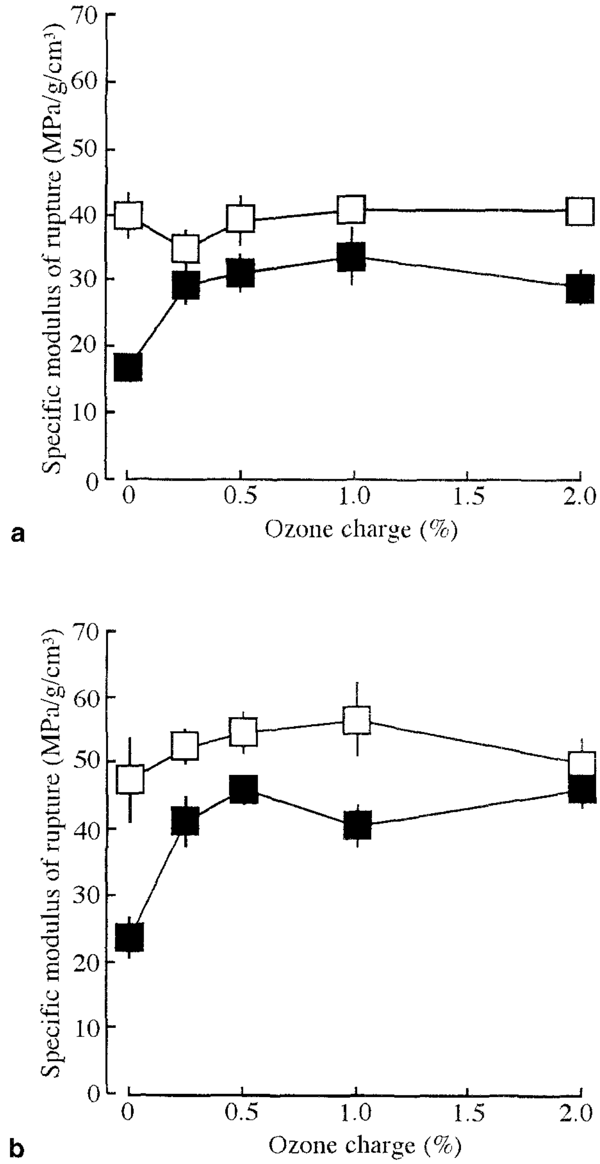

Fig. 4. Relations between ozone charge and specific modulus of rupture (MOR/mean board density). **a** Low-density board, 0.5 g/cm^3 target board density. **b** Medium-density board, 0.7 g/cm^3 target board density. *Open squares*, unacetylated boards; *filled squares*, acetylated boards. *Vertical lines* denote standard deviations

Bending strength

High bending strength is probably expected with high IB. Figure 4 shows the relations between ozone charge and specific MOR (MOR/mean board density).[15] The specific MOR of almost all the boards increased from 0% to 0.5%–1.0% ozone charge. The ozonation of acetylated boards, in particular, was more effective than that of unacetylated boards. The specific MOR of almost all the boards did not increase with an ozone charge over 1.0%. Thus, an effective ozone charge of 0.5%–1.0% was obtained. Takata et al. reported that the optimum ozone charge for bending strength was 0.25%–0.50%, and that an excessive ozone charge might weaken the cellulose.[5] At high ozone charges, the bending strength reported by Takata et al. decreased more than did that in our study. This difference may be due to the difference in raw material. Their boards were made from waste paper.

The MOR is related to face density (Table 2).[11] The relations between face density and MOR are shown in Fig. 5. The MOR increased with increasing face density. In particular, the face density of the acetylated medium-density boards increased considerably at high ozone charges. This is also one of the reasons for increased MOR. Although excessive ozone charge may weaken the acetylated fibers, the increasing face density and bonding strength probably overcomes the deterioration of fibers.

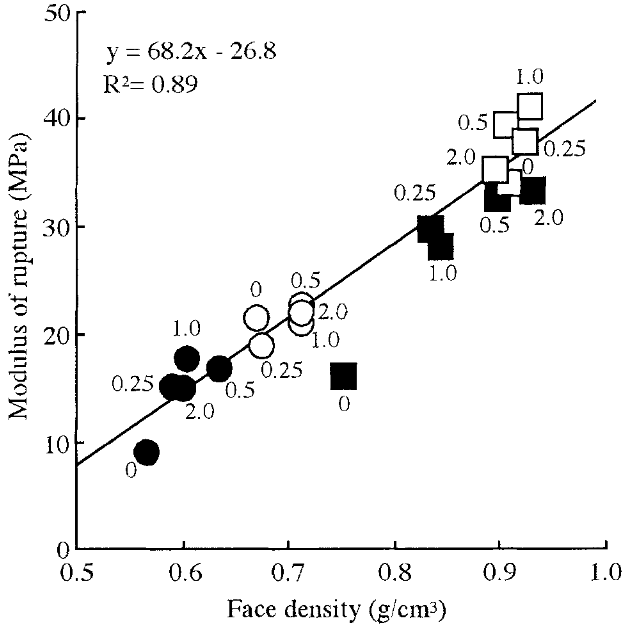

Fig. 5. Relations between face density and modulus of rupture. *Open circles*, unacetylated low-density board (0.5 g/cm^3 target board density); *filled circles*, acetylated low-density board (0.5 g/cm^3 target board density); *open squares*, unacetylated medium-density board (0.7 g/cm^3 target board density); *filled squares*, acetylated medium-density board (0.7 g/cm^3 target board density). The numbers in the graph indicate the ozone charge. Regression line is indicated in the graph. Refer to Fig. 1 and Table 2 for an explanation of face density

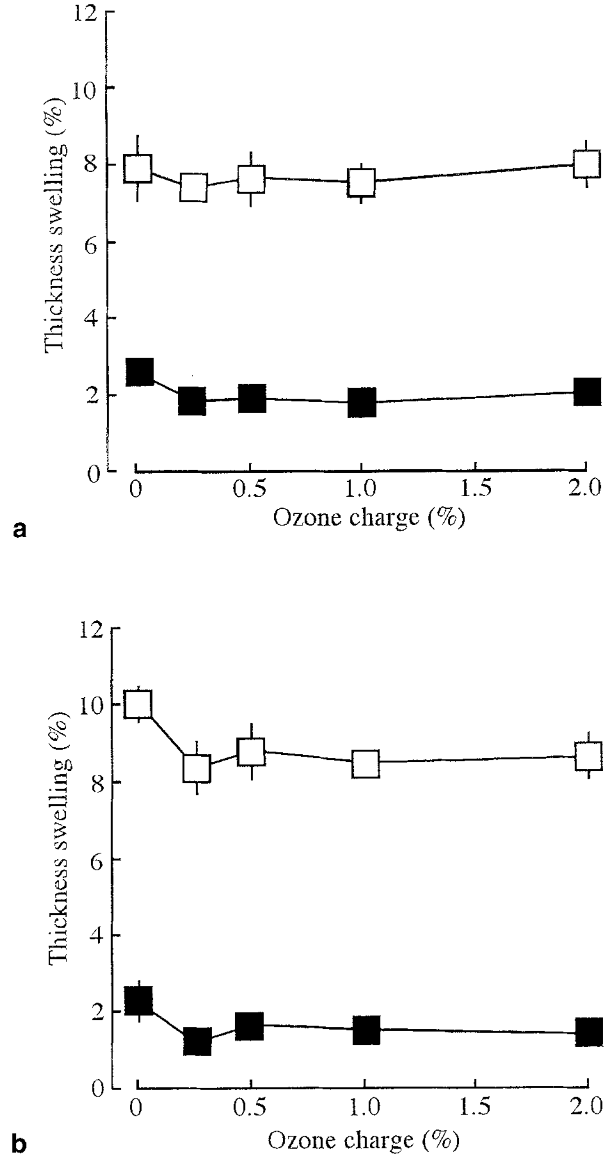

Fig. 6. Relations between ozone charge and thickness swelling. **a** Low-density board, 0.5 g/cm^3 target board density. **b** Medium-density board, 0.7 g/cm^3 target board density. *Open squares*, unacetylated boards; *filled squares*, acetylated boards. *Vertical lines* denote standard deviations

Thickness swelling

Figure 6 shows the relations between ozone charge and TS. The ozonation improved the TS except in unacetylated low-density boards. Again, a low compaction ratio did not exhibit effective ozonation.

Conclusions

Ozone cleaves the aromatic rings of lignin and introduces carboxyl groups; hence the wettability and thermoplasticity of acetylated fibers increase. This increased wettability and thermoplasticity improves the interfiber contact, resulting in increasing internal bond and bending strength. In addition, the thermoplasticity leads to high face density, which also improves the bending strength. The high compaction ratio accelerates the effect of ozonation. In every aspect, 0.5%–1.0% ozone charges improve the properties of acetylated fiberboards.

Acknowledgments The authors thank Mr. A. Ito of Mitsui Chemical Co. for supplying the adhesive, and Mr. K Shimada, Mr. K. Kawarada, and Mr. T. Iida of Tokyo Metropolitan Industrial Technology Research Institute for measuring the contact angle. They also extend thanks to Mr. Y. Hiramatsu, Dr. A. Inoue, Dr. T. Tomimura, Dr. K. Magara, Dr. Ikeda, Dr. M. Ohkoshi, and Dr. Y. Hatano of Forestry and Forest Products Research Institute and Mr. T. Matsuda and Mr. Y. Chiba of the former Forestry and Forest Products Research Institute.

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