Transposition of Chrome Tanning in Leather Making

by

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Abstract

To avoid the release of chrome from leather into post tanning effluents and the generation of chrome shavings, an inverse chrome tanning technology based on wet white was investigated. Conventional bated pelt was firstly tanned using an amphoteric organic tanning agent (Tingjiang white tanning agent, TWT) without pickling. Then, the TWT tanned wet white was directly processed with conventional post tanning processes. Chrome tanning was transposed to the end of the post tanning. The wet white had a shrinkage temperature (Ts) around 85°C that met the needs of shaving operation, and did not generate chrome shavings. The Ts and Cr_2O_3 content of the leather, by using this inverse chrome tanning technology, were higher than those of the conventional chrome tanned leather. With this inverse technology, the chrome output was reduced by 48%, mainly because no chrome was released from leather in post tanning processes. Meanwhile, the volume of chromium-containing wastewater discharged from the inverse processes was barely 31% of that from the conventional processes, which makes it much easier to collect and recover chromium from the effluents. Additionally, the tensile strength, tear strength and general appearances of the leather produced by the inverse technology were comparable to those of the conventional chrome tanned leather.

Introduction

Chrome tanning is the most widely used tannage in leather industry, because it can endow leather with a comfortable feel and high hydrothermal stability. Furthermore, compared with chrome free tannages, chrome tanning is more suitable for production of diverse leathers, and chrome tanned crust leather has better compatibility with retanning and fatliquoring chemicals.[1] However, the conventional chrome tanning system brings about excessive discharge of chromium into effluents as well as abundant chrome shavings.[2] The discharge of chromium into effluents results from incomplete absorption of chrome powder (40%~70%) in chrome tanning process[3] and release of free and unstably combined chrome from leather during post tanning processes.[4, 5] Post tanning processes mainly include rewetting, retanning, neutralizing, dyeing and fatliquoring processes, which are performed after chrome tanning to improve the handle and feel of the leather and to change the color of the chrome tanned leather. As for chrome tanning process, high exhaustion chrome tanning,[6] recovery of chromium from chrome tanning liquor,[7] and recycling of chrome tanning liquor[8] are all efficient in reducing the discharge of chromium. But, it is worth noting that the release of chrome from leather in post tanning processes causes the chrome content in each post tanning effluent to far exceed the discharge standard, and results in a significant increase in volume of chrome-containing wastewater.[5] In fact, it is nearly impossible to recover chromium from all the post tanning effluents in consideration of technical difficulty and costs. Hence, to meet the increasingly stringent standard of chromium discharge (0.3~2.0 mg/L in many countries),[9] much research has recently focused on the development of environmentally friendly tanning systems.

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Wet white technology is useful to eliminate chrome shavings by providing chrome free tanned crust leather for shaving operation.[10] However, the following semi-chrome tanning process still results in the release of chrome from leather during post tanning processes. In fact, once chrome tanned leather is processed in post tanning processes, the release of chrome from leather into post tanning effluents will be an inevitable result. Accordingly, it is reasonable to infer that the only solution to the release of chrome into post tanning effluents is to undertake chrome tanning after post tanning processes. In this way, only last one process generates chrome-containing effluent in the whole leather making processes, which certainly favors effective treatment/recovery of chrome in tannery. Saravanabhavan *et al*. has reported a reversed leather making technology where bating process was promptly followed by post tanning processes, and chrome tanning was carried out at the end.[11] However, because the purpose of the reversed technology was just to simplify leather making processes and to reduce pollution and water consumption, chrome tanning was directly performed in the float of post tanning, which makes it difficult to recover chromium from dye and fatliquor-containing wastewater. Furthermore, the bated pelts used for post tanning processes cannot be stored or shaved to an even thickness due to their low hydrothermal stability.

In order to achieve a more reasonable transposition of chrome tanning in leather making, it is necessary to provide post tanning processes with suitable crust leather that possesses enough hydrothermal stability and great affinity for anionic post tanning chemicals. In our previous work, a wet white technology based on an amphoteric organic tanning agent (Tingjiang white tanning agent, TWT) was developed, where TWT included amino, carboxyl and aldehyde groups. The wet white tanned by TWT has enough hydrothermal stability (shrinkage temperature (Ts) = 83~86^{o}C) to be stored or shaved.[12] Additionally, compared with wet white tanned by using organic phosphonium salts, oxazolidine or modified glutaraldehyde, the wet white tanned with TWT can take up more anionic dyestuffs and fatliquors because of the amphoteric property of TWT.[12] Hence, the wet white tanned with TWT would be a satisfactory intermediate tanned leather to be provided for post tanning processes.

In this paper, an inverse chrome tanning technology based on wet white was investigated. Firstly, conventional bated pelt was tanned by using TWT without pickling. Then, the TWT tanned wet white was processed with conventional post tanning processes. At the end, chrome tanning was performed to improve hydrothermal stability and feel of the leather. The discharged chrome in all the effluents and the properties of the leather produced by using the inverse chrome tanning technology were determined and compared with those by using conventional leather making processes.

EXPERIMENTAL

Materials

Common limed cowhide (thickness 1.8 mm), chrome powder (22% Cr_2O_3, 33% basicity) and the amphoteric organic tanning agent (TWT) prepared by the method described in our previous paper[12] were used for leather making trials. All the chemicals used for leather processing were of commercial grade and the chemicals employed for analyses of leathers and effluents were of analytical grade.

Leather Making Processes

Two limed pelt samples (dimensions 50 cm × 50 cm) were cut from back region of the limed cowhide and weighed. They were then delimed, bated and washed by common procedures. Subsequently, they were processed by using the procedures given in Table I and Table II, respectively. At the end of each process, pH of effluent was measured by precise pH meter. In addition, leather samples and effluent samples were collected for analyses, as shown in Table I and Table II.

Analyses of Leather Properties

Hydrothermal Stability

The hydrothermal stability of leathers (No. 1, 2, 3, and 4) was evaluated by measuring shrinkage temperature (Ts) using a standard shrinkage temperature recording instrument.

Distribution of Chrome in Leather

Leathers No. 2 and 4 were equally split into three layers and then dried to constant weight. 50 mg of each dried sample was digested by 10mL of aqua regia, and the concentration of chrome in the digestion liquor was subsequently determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Optima 2100DV, PerkinElmer, USA). The chrome content of each layer was calculated as:

$$\text{chrome content} = \frac{Cr_2O_3 \text{ weight in chrome leather}}{\text{dry weight of chrome leather}} \times 100\% \quad (1)$$

The distribution of chrome in leather was assessed by comparing the chrome contents of three layers.

Morphology of Leather

The grain surfaces of leathers No. 2 and 4 and their cross sections were observed by using Field Emission Scanning Electron Microscope (FESEM, JSM-7500F, JEOL, Japan).

Physical Properties

Leathers No. 2 and 4 were first conditioned at 20^{o}C and 65% relative humidity for 48 h, and then their physical properties such as tensile strength and tear strength were tested according to ASTM standard method. Sensory properties of the leathers were assessed by softness, fullness, grain smoothness and grain tightness. Each sensory property was graded on a scale of 0~5 by three experienced tanners without knowing the production process of each leather.

TABLE I
Inverse chrome tanning for leather making.

Process	Chemical	Temperature (ºC)	Offer (%)	Time (min)	Remark
Washing[a]	Water	25	200	10	
Chrome free tanning[a]	Water	25	80		
	TWT		7	120	pH 7.0-7.5
	Water	40	100	240	Leather sampling (No. 1). Piled overnight.
Samming, shaving and weighing[b]					
Rewetting	Water	30	200		
	Formic acid		0.3	30	pH 5.0-5.5, drain.
Retanning	Water	30	150		
	Synthetic fatliqour/ Dispersing syntan		1/2	30	
	Acrylic resin		3	30	Adjust pH to 4.5-5.0.
	Mimosa		6	90	
	Phenolic syntan/ Melamine resin		4/3	60	
	Formic acid		1	30	pH 4.5
Fatliquoring	Water	50	100		
	Synthetic fatliqour		10	60	
	Formic acid		1.5	3 x 15 min	Effluent sampling (No. 1). pH 3.8, drain.
Chrome tanning	Water	35	100		
	Chrome powder		14[c]	120	Check for penetration.
Basifying	Sodium formate		1		
	Sodium bicarbonate		1.5	3 x 30 min	pH 3.8-4.0
	Water	40	100	240	Effluent sampling (No. 2).
Washing	Water	25	200	15	Effluent sampling (No. 3). Piled overnight.
Horse up, samming, hang-drying overnight, and staking. Leather sampling (No. 2).					

[a]The percentage of chemical was based on the weight of limed pelt.
[b]The water content of wet white was 55%.
[c]The offer of chrome powder was the same as the total offer used in chrome tanning and retanning listed in Table II.

TABLE II
Conventional chrome tanning for leather making.

Process	Chemical	Temperature (°C)	Offer (%)	Time (min)	Remark
Pickling[a]	Water	25	60	10	
	Sodium chloride		7	20	
	Formic acid		0.8	30	
	Sulfuric acid		0.6	3 x 15 min	pH 2.6-2.8
				240	Rest overnight.
Chrome tanning[a]	Chrome powder	25	5	240	
Basifying[a]	Sodium formate	25	1.5	30	
	Sodium bicarbonate		1.5	4 x 20 min	pH 4.0-4.2
	Water	40	100	360	Leather (No. 3) and effluent (No. 4) sampling. Piled overnight.
Samming, shaving and weighing[b]					
Rewetting	Water	30	200		
	Formic acid		0.3	40	pH 3.5-3.7 Effluent sampling (No. 5). Drain.
Chrome retanning	Water	30	100		
	Chrome powder		4	120	
Basifying	Sodium formate	30	1.2	30	
	Sodium bicarbonate		0.8	3 x 20 min	pH 4.0-4.2.
	Water	40	50	240	Effluent sampling (No. 6). Drain.
Washing	Water	25	150	10	Effluent sampling (No. 7). Drain.
Neutralizing	Sodium formate	30	1.5	60	
	Sodium bicarbonate		0.8	30	pH 5.0-5.5. Effluent sampling (No. 8).
Retanning & Fatliquoring	The leather was retanned and fatliquored by using the same procedures given in Table I. Effluent sampling (No. 9).				
Horse up, sammimg, hang-drying overnight, and staking. Leather sampling (No. 4).					

[a]The percentage of chemical was based on the weight of limed pelt.
[b]The water content of wet blue was 55%.

Analyses of Effluents

Total Organic Carbon (TOC) Concentration

Effluents No. 1 and 9 were filtered and the filtrates were taken for the measurement of TOC concentration (named residual TOC concentration) by TOC / TN analyzer (LiquiTOC, Elementar, Germany). The retanning and fatliquoring chemicals were added in the same float as shown in Table I without leather, and the TOC concentration of the float was measured as an initial TOC concentration. The absorption extent of TOC by leather was chosen to evaluate the absorption capacity of leathers to retanning and fatliquoring chemicals and calculated as:

$$\text{absorption extent of TOC by leather} = \frac{\text{initial TOC - residual TOC}}{\text{initial TOC}} \times 100\% \quad (2)$$

Concentration of Chrome in Effluents

Effluents No. 2-9 were taken for the determination of chrome concentration. 3 mL of the effluent was digested by 10mL of aqua regia, and then the concentration of chrome in the digestion liquor was determined using ICP-AES. The chrome content per unit volume of effluent was calculated.

Results and Discussion

pH Change in Leather Making Processes

In leather making processes, ionic charge of pelt/leather is an important factor influencing the penetration rate and the fixation extent of chemicals in pelt/leather, and therefore tanners generally control the reactions between pelt/leather and chemicals by adjusting the pH of pelt/leather. In conventional leather making processes, chrome tanning needs an initial pH of 2.6~3.2 to promote the penetration rate of chromium in pelts, while retanning and fatliquoring usually require an initial pH of 5.0~6.0 to increase the penetration rate of organic chemicals. Hence, pickling is an indispensable process after bating to achieve the pH of 2.6~3.2 for chrome tanning, and neutralizing has to be carried out to increase the pH of leather to 5.0~6.0 for retanning and fatliquoring (Figure 1(a)). Unfortunately, the processes such as pickling and neutralizing not only complicate the leather making technology, but also generate a great quantity of salts in wastewater.

In the inverse leather making processes as described in Table I, bated pelt was directly employed for tanning since the proper pH for TWT tanning was 7.0~8.0.[12] As a result, the pickling process was omitted, and the pH of pelt/leather was gradually reduced to the required values for retanning and fatliquoring (Figure 1(b)), which simplify the operations and diminish the generation of salts.

Content and Distribution of Cr_2O_3 in Leather

Leather is normally sammed and then shaved to a required thickness before retanning, and therefore it should possess an enough hydrothermal stability to avoid damage from these mechanical operations.[13] In this study, the hydrothermal stability of the wet white and the wet blue was evaluated by Ts measurement. The results showed that the Ts of the wet white was 85°C, while that of the wet blue was 103°C. Obviously, the Ts of the wet white was lower than that of the wet blue, but it was high enough for shaving operation and storage.

It is interesting that the Ts of the leather produced by the inverse technology (124°C) was slightly higher than that of the leather produced by the conventional technology (120°C). Furthermore, in comparison with the conventional leather, the leather produced by using the inverse technology had higher Cr_2O_3 content and more uniform distribution of Cr_2O_3 in each layer (see Table III). These results suggest that the inverse technology is beneficial to the penetration and fixation of chrome in leather. These phenomena may be due to the fact that the pH of leather after fatliquoring (pH 3.8) is fit for the

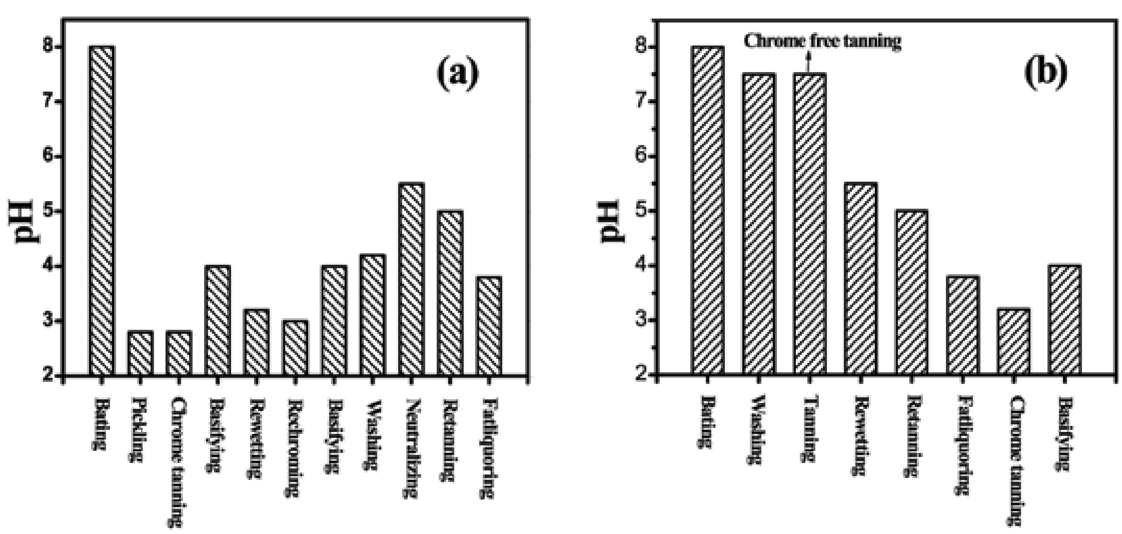

Figure 1. pH of pelt/leather in conventional leather making processes (a) and inverse leather making processes (b).

penetration of chrome in the post-tanned wet white, and that the reactive groups provided by retanning agents, such as phenolic hydroxyl and carboxyl groups, can improve the fixation of chrome in leather.[14]

TABLE III
Content of Cr_2O_3 in inverse and conventional resultant leathers.

Sample of leather	Grain layer (%)	Middle layer (%)	Flesh layer (%)	Average (%)
No. 2 - Inverse	4.56	4.57	4.53	4.55
No. 4 - Conventional	3.93	3.85	3.90	3.89

Discharge of Chrome from Leather Making Processes

In the inverse chrome tanning technology, chrome was only discharged into the effluents in the last chrome tanning and the subsequent washing processes. As shown in Table IV, only 4.0 ton of chromium-containing wastewater was generated when 1.0 ton of wet white was processed. In the conventional technology, according to Table V, it is obvious that the free and unstably combined chrome in leather was released into all the effluents of post tanning processes, and that the content of chrome in each effluent far exceeded the discharge standard,[9] which were consistent with the results obtained in previous studies.[5] As a result, 13.0 ton of wastewater containing approximately 6.6 kg of chromium was discharged when 1.0 ton of wet blue was processed. Comparing Table IV and Table V, it is found that the chrome output can be reduced by 48% when chrome tanning is performed after fatliquoring, because the release of chrome from leather during post tanning processes is eliminated. The elimination of chrome release in post tanning processes should be the main reason that Cr_2O_3 content in the leather by using inverse technology is higher than that by using conventional technology. Moreover, the

TABLE IV
Discharge of chrome from the inverse leather making processes.

Sample of effluent	Concentration of chrome (mg/L)	Amount of effluent (ton)	Chrome output/(g/ton wet white)
No. 2 - Chrome tanning	1210	2.0	2420
No. 3 - Washing	500	2.0	1000
Total	/	4.0	3420

TABLE V
Discharge of chrome from the conventional leather making processes.

Sample of effluent	Concentration of chrome (mg/L)	Amount of effluent (ton)	Chrome output/ (g/ton wet blue)
No. 4 - Chrome tanning	920	4.0	3680
No. 5 - Rewetting	167	2.0	334
No. 6 - Chrome retanning	975	1.5	1463
No. 7 - Washing	458	1.5	687
No. 8 - Neutralizing	183	1.5	275
No. 9 - Retanning and Fatliquoring	75	2.5	188
Total		13.0	6627

volume of chromium-containing wastewater discharged from the inverse technology was barely 31% of that from the conventional technology. The significant decrease in the volume of chromium-containing wastewater makes it much easier to collect and recover chromium from the effluents.

Absorption Capacity of Leathers to Retanning and Fatliquoring Chemicals

In order to obtain required properties of leather for end-uses, it is essential to correctly complete retanning and fatliquoring processes. The successful performance of retanning and fatliquoring first needs a good absorption capacity of leather to retanning agents and fatliquors. Therefore, the absorption capacity of leathers to retanning and fatliquoring chemicals was evaluated by determining the residual TOC concentration in effluent after fatliquoring, where the retanning and the fatliquoring were carried out in the same float. As shown in Table VI, the residual TOC concentrations in the fatliquoring effluents of the two technologies were nearly the same. This result means that the absorption capacity of the wet white to retanning agents and fatliquors is as high as that of the wet blue, which is due to the amphoteric property of TWT as mentioned earlier.[12] Based on the high absorption capacity of the wet white to retanning and fatliquoring chemicals, it is likely that the properties of the leather based on inverse technology are similar to those of the conventional leather.

Morphology of Leathers

The surface morphology of the leathers produced by inverse and conventional technologies was observed by FESEM, as shown in Figure 2(a) and 2(b). The grain surfaces of both leathers were clear. The leather by using inverse technology has a more compact surface (Figure 2(a)) compared with the conventional leather (Figure 2(b)), which may be due to the fact that a higher Cr_2O_3 content in the former improved the astringency of surface. The stronger astringency may lead to an area loss of leather by using inverse technology, but it can be modified by changing the offer of chrome powder. The FESEM photos of cross sections of the leathers are given in Figure 2(c) to 2(f). The dispersed extents of collagen fiber bundles of the leathers based on two technologies were very similar.

TABLE VI
TOC concentration of effluents from inverse and conventional fatliquoring processes.

Sample of effluent	Initial TOC (mg/L)	Residual TOC (mg/L)	Absorption extent of TOC by leather (%)
No. 1 - Inverse	25300	5620	77.8
No. 9 - Conventional	25300	5450	78.5

Physical Properties of Leathers

Tensile strength and tear strength are important mechanical properties of leather for its application. As listed in Table VII, the tensile strength and tear strength of the leather by using inverse technology was comparable to those of the conventional leather. Since the tensile strength and tear strength mainly depend on tanning method, flexibility of collagen fiber, dispersion of collagen fiber and weave pattern of collagen fibers in leather,[15-17] it can be inferred that the leather tanned using inverse technology was similar to the conventional leather in the above-mentioned aspects. The sensory properties of the leathers were assessed by subjective evaluation of softness, fullness, grain smoothness and grain fullness, as shown in Figure 3. The leather, by using inverse technology, exhibited slightly better fullness and grain tightness compared with the conventional leather. However, the grain smoothness of the leather, by using inverse

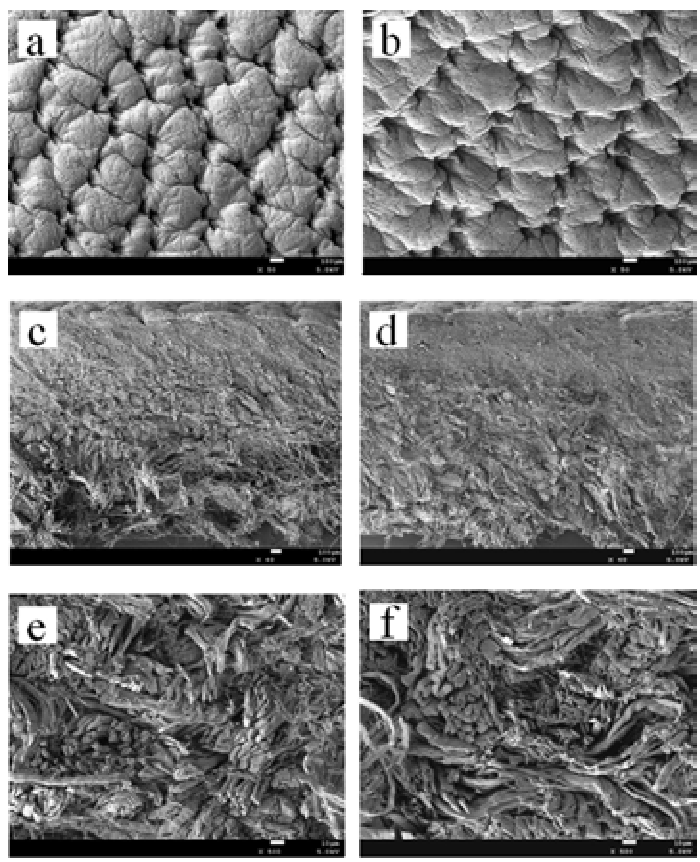

Figure 2. Grain surfaces of leathers observed by FESEM at a magnification of 50x: (a) inverse technology, (b) conventional technology; cross sections of leathers at a magnification of 45x: (c) inverse technology, (d) conventional technology; cross sections of leathers at a magnification of 500x: (e) inverse technology, (f) conventional technology.

technology, was a little worse, which was consistent with the result observed in the FESEM photos. In summary, the general appearances of both the leathers were almost the same.

TABLE VII
Tensile strength and tear strength of the final leathers.

Sample of leather	Tensile strength (N/mm^2)	Tear strength (N/mm)
No. 2 - Inverse	11.2	40.2
No. 4 - Conventional	10.5	38.5

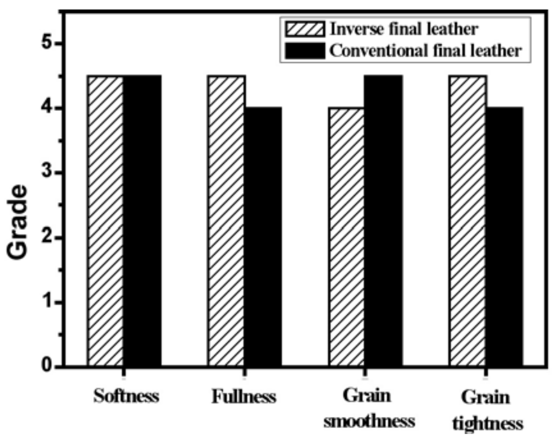

Figure 3. Evaluation of sensory properties of the resultant leathers.

CONCLUSIONS

The inverse chrome tanning technology based on wet white is effective in avoiding the generation of chrome shavings and the release of chrome from leather during post tanning processes. The significant advantage of this technology is the fact that it can dramatically reduce waste of chrome and the volume of chromium-containing wastewater, which would largely favor the full collection and recovery of chromium discharged in leather making. Of course, the wide suitability of this technology should be further investigated, although this research demonstrated that the properties of leather made by the inverse chrome tanning technology are comparable to those of the conventional chrome tanned leather.

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